Posters

Foliar Nitrogen Status and Growth of Plants Exposed to Atmospheric Ammonia (NH_3)

Adrizal[1], P.H. Patterson[1], R.M. Hulet[1], and R.M. Bates[2]

[1]Department of Poultry Science, and [2]Department of Horticulture, Penn State University, University Park, PA 16802

Abstract

Two experiments were conducted to evaluate the potential of plant species to trap NH_3 discharged from poultry houses. The four plant species (cedar, locust, poplar, and grass) used in experiment (Exp) 1 and four species (spruce, arborvitae, poplar, and willow) used in Exp 2 were transplanted into 4- to 8-L pots and grown in four environmentally controlled chambers. Two of the four chambers received continuous anhydrous NH_3 at 4 to 5 ppm (Exp 1) or 6 to 8 ppm (Exp 2) while the other two chambers in each experiment received no NH_3. The results of Exp 1 showed that locust was the fastest growing species, supported by its total biomass, root, and root DM weights. There was a trend for all the plants exposed to NH_3 to have greater leaf DM than their non-exposed counterparts at 6 (43.0 vs. 30.8%; $P=0.09$) and 12 wk (47.9 vs. 36.6%; $P=0.07$), and significantly greater ($P \leq 0.05$) leaf N at 6 (6.44 vs. 3.67%) and 12 wk (7.05 vs. 3.51%) when exposed to NH_3. An increase in leaf N due to NH_3 exposure was also noted in Exp 2 (4.99 vs. 2.83%; $P \leq 0.05$), but with no indication with species interaction. Numerically greater leaf DM due to NH_3 exposure was consistently measured in poplar tissues at both sampling periods in Exp 1. In Exp 1, poplar, as well as locust and grass, deposited 1.5 to 2 fold greater N in their leaves than cedar tissues as a result of NH_3 exposure compared to non-exposed plants. Similar numerical trends in foliar N were also observed in poplar, willow and arbovitae in Exp 2 ($P > 0.05$). Locust (Exp 1) likely benefited from ambient NH_3 while poplar and willow (Exp 1 and 2) were negatively affected by atmospheric NH_3.

Introduction

Ammonia (NH_3) is the foremost gas of concern in poultry houses. Feed can be a major contributor of this gas since NH_3-N losses as a percentage of dietary feed-N range from 18 to 40% depending on type of bird (broiler, turkey, pullet, or laying hen) (Patterson and Lorenz, 1996, 1997, Patterson et al., 1998; Patterson et al., 1999), age, and management style. Both dietary and in-house management strategies are utilized to reduce the generation and emission of NH_3 inside the house, but offer no benefit once it is discharged via the exhaust fans. Field observations since 2003 on Pennsylvania poultry farms indicate that neighbors are concerned about emissions around many poultry production sites (unpublished data). However, concentrations of the airborne NH_3 once it is discharged by the exhaust fans is not well documented, and is dependent on the fan performance, outside wind speed, distance of measurement from the exhaust fan, and the presence of vegetation (Seedorf and Hartung, 2000; Pitcairn et al., 1998).

Yin et al. (1998) reported it is possible for atmospheric NH_3 to enter plants through foliar stomata and assimilate into plant cells through the glutamine synthetase and glutamate synthase pathways at up to 5.51 ppm NH_3 for short periods of time without disturbing photosynthesis or transpiration. Hence, at favorable concentrations, NH_y ($NH_3 + NH_4^+$) will induce plant growth while at a critical threshold NH_3 will cause necrosis, growth reduction, and increased frost sensitivity (Van deer Eerden et al., 1998). The objective of this study was to evaluate the tolerance of some plant species to NH_3 exposure released at a concentration range commonly detected near commercial poultry farms.

Materials and Methods

Four plant species were grown in environmentally controlled chambers up to 12 wk in Experiment (Exp) 1 or 6 wk in Exp 2. The plants comprised of 53 four-yr-old red cedar (*Juniperus virginiana*), 40 one-yr-old thornless honey locus (*Gleditsia triacanthos* var. *inermis*), 57 one-yr-old hybrid poplar (*Populus sp*.), and 58 uniform of clumps of reed canary-grass (*Phalaris arundinacea*) in Exp 1. In Exp 2 45 3-yr-old white spruce (*Picea glauca*), 45 3-yr-old arbovitae (*Thuja spp*.), 46 two-yr-old poplar, and 32 two-year-old streamco willow (*Salix purpurea*) were utilized. All the plants were transplanted into 4- and 8-L pots containing NX-6 pine bark media and placed onto two tables in each chamber. Two of the four chambers were treated with (+) NH_3 exposure at 4 to 5 ppm (Exp 1) or 5 to 7 (Exp 2) and the other two in each experiment received no (-) NH_3. Each plant species in each chamber of Exp 1 was divided into two groups with no fertilizer (-) or NPK fertilizer at 100 ppm (+) once a week. All plants in Exp 2 received the fertilizer.

The anhydrous NH_3 was released from a 150-L NH_3 tank via a flow meter, monitored by a photoacoustic NH_3 detector (Model 1412, Innova, DK-2750 Ballerup, Denmark) weekly and backed-up with passive dosi-tube readings (3D, Gastec Corp., 6431 Fukaya, Japan). The lighting program was set for 16 h light and 8 h dark (16L:8D) every day for all chambers and light intensity was maintained at minimum (Exp 1) or medium requirements (Exp 2). Chamber temperature (T) and relative humidity (RH) were programmed to meet the required level for plant growth. Two fertilized plants per species per chamber were sampled on wk 0, 6, (Exp 1 and 2), and 12 (Exp 1) for fresh plant biomass wt, root wt, root DM, foliar DM and N analyses. Plant height and stem diameter were recorded on all plants only in Exp 1.

Data were subjected to a split plot design analysis of Proc Mixed of SAS (SAS Institute, 1999). Model 1 was used to analyze foliar DM and N data of Exp 1 and 2, while Model 2 was used to analyze plant height and plant diameter data obtained from Exp 1. The two models are as described below:

$$X_{ijk} = \mu + A_i + C(A_i)_j + S_k + AS_{ik} + \varepsilon_{(ijk)} \ldots\ldots\ldots\ldots \quad \text{(Model 1)}$$

$$X_{ijkl} = \mu + A_i + C(A_i)_j + S_k + F_l + AS_{ik} + AF_{il} + SF_{kl} + ASF_{ikl} + \varepsilon_{(ijkl)} \ldots\ldots \quad \text{(Model 2)}$$

where X_{ijk} or X_{ijkl} is the value observed, μ is the overall mean, A is the effect of NH_3 (main plot factor), C(A) is the error for A (where C = chamber, which is nested in A), S and F are the effects of species and fertilizer (sub plot factors), respectively, AS is the interaction effect of NH_3 by species, AF is the interaction effect of NH_3 by fertilizer, SF is the interaction effect of species by fertilizer, ASF is the interaction effect of NH_3 by species by fertilizer, and ε is the residual error. Tukey's test (SAS Institute, 1999) was employed to the data showing significance ($P \leq 0.05$).

Results

The average daily T and RH ranged from 24 to 24.7 ºC and 44.3 to 44.7%, in the (-) and (+) NH_3 chambers, respectively in Exp 1, while in Exp 2 they were 24.2 to 24.7 ºC and 44.8 to 45%, respectively. Light intensity averaged 1522 lux in Exp 1 and 3049 lux in Exp 2. The concentrations of NH_3 ranged from 0.08 to 0.20 ppm in the (-) NH_3 chambers (Exp 1 and 2) and 4 to 5 ppm (Exp 1) and 6 to 8 ppm (Exp 2) in the (+) NH_3 chambers.

Experiment 1

Species had a significant effect ($P \leq 0.05$) on plant height and stem diameter in Exp 1 (Table 1). Although the significant effect of species by fertilizer at 6 wk existed ($P \leq 0.05$) it did not indicate a trend of plant height with fertilizer. Species was the only factor to influence total fresh biomass wt and fresh root wt (Figure 1) at all weeks in Exp 1 ($P \leq 0.05$). A significant effect of species was also observed on plant root DM. An increased root DM due to the interaction of NH_3 by species was only numerical particularly in locust (46.7 to 56.1%) at 12 wk (data are not shown).

There was a repeatable trend of the NH_3 treatment to increase leaf DM at 6 ($P=0.09$) and 12 wk ($P=0.07$) and a highly significant NH_3 effect on N deposition in plant foliage at both weeks (Table 2). Leaf DM content appeared to be positively impacted by the NH_3 treatment in the case of red cedar and hybrid poplar at week 6 ($P=0.07$) and upon hybrid polar at 12 wk ($P=0.06$) but not so for locust or reed canary grass. Moreover, the NH_3 by species interaction was highly discernable in leaf N levels with greater concentrations at 6 and 12 wk for locust, poplar, and grass as a result of NH_3 exposure. Total foliar N of the fresh leaf material at 6 and 12 wk was calculated by difference between control (-) and (+) NH_3 chambers to be 0.45 and 0.87 g 100 g^{-1} of fresh foliage weight for grass, 1.25 and 1.34 g for locust, and 2.67 and 6.09 g for poplar based on the leaf DM and N concentrations reported in Figure 2.

Table 1. Plant heights and stem diameters of plants treated with (+) or without (-) atmospheric ammonia (NH_3) for 12 wk, Exp 1.

Treatment	Height (cm)			Stem Diameter[2] (cm)		
	Wk 0	Wk 6	Wk 12	Wk 0	Wk 6	Wk 12
NH_3: (-)	53.8	66.0	68.5	0.72	0.70	0.70
(+)	53.4	65.1	65.4	0.74	0.70	0.71
Species (Spec):						
Red cedar (R)	48.2^{b}	46.3^{c}	46.9^{c}	0.87^{a}	0.77^{a}	0.78^{a}
Honey locust (L)	54.6^{ab}	83.1^{a}	88.0^{a}	0.60^{b}	0.62^{b}	0.64^{b}
Hybrid poplar (P)	57.8^{a}	69.0^{b}	68.7^{b}	0.71^{b}	0.71^{b}	0.69^{b}
Reed canary grass (G)	53.9^{ab}	63.8^{b}	64.2^{b}	-	-	-
Fertilizer (Fert): (+)	52.7	66.0	67.8	0.71	0.67	0.68
(-)	54.5	65.1	66.1	0.74	0.73	0.73
Spec x Fert:						
R × (+)	48.6	45.0^{e}	45.2	0.86	0.72	0.74
R × (-)	47.8	47.5^{de}	48.5	0.88	0.81	0.81
L × (+)	54.1	85.7^{a}	92.8	0.57	0.61	0.65
L × (-)	55.0	80.5^{ab}	83.3	0.63	0.62	0.64
P × (+)	54.1	64.8^{bc}	65.7	0.70	0.66	0.65
P × (-)	61.5	73.1^{abc}	71.7	0.72	0.77	0.73
G × (+)	54.1	68.3^{bc}	67.4	-	-	-
G × (-)	53.7	59.3^{cd}	61.0	-	-	-
NH_3 × Spec:	…[1]	…	…	…	…	…
NH_3 × Fert:	…	…	…	…	…	…
NH_3 × Spec × Fert	…	…	…	…	…	…
Sources of Variances:	Probabilities					
NH_3	0.94	0.71	0.52	0.80	0.90	0.72
Spec	0.04	0.0001	0.0001	0.0002	0.03	0.04
Fert	0.45	0.71	0.57	0.51	0.14	0.27
Spec × Fert	0.53	0.05	0.19	0.94	0.65	0.62
NH_3 × Spec	0.83	0.95	0.21	0.91	0.42	0.71
NH_3 × Fert	0.64	0.11	0.07	0.74	0.91	0.45
NH_3 × Spec × Fert	0.52	0.83	0.82	0.93	0.98	0.82

[a-e] Means in a column with no common superscripts differ significantly ($P \leq 0.05$).

[1] Mean values are not shown because they did not have significant probabilities ($P \geq 0.05$).

[2] Measuremens were taken only on red cedar, honey locust, and hybrid poplar.

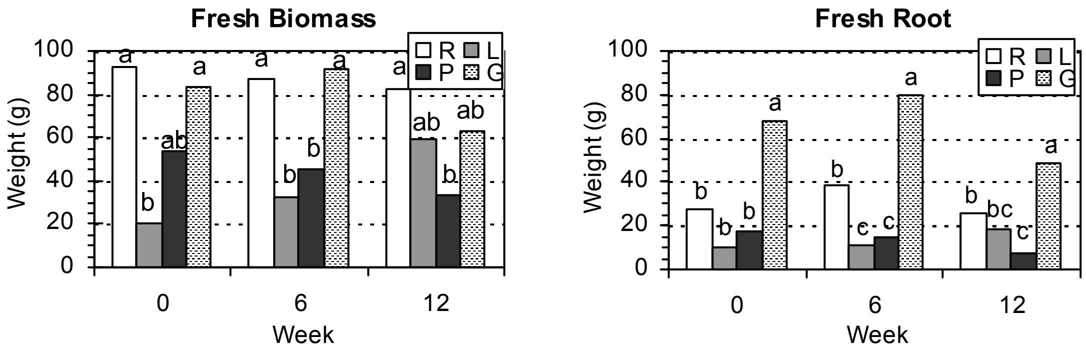
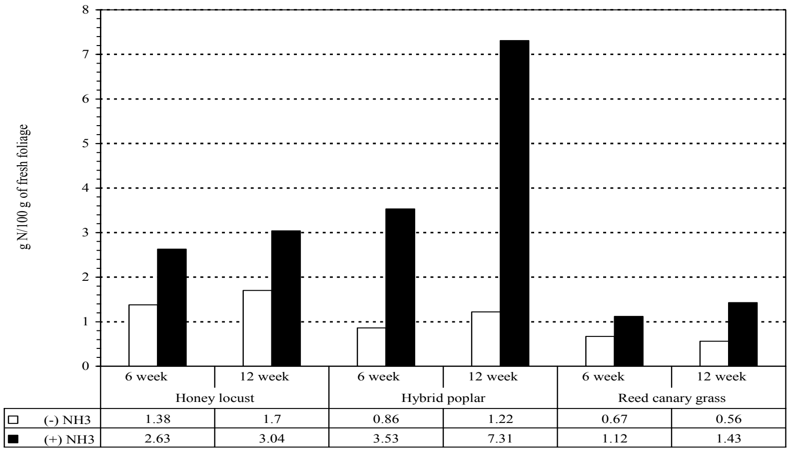


Figure 1. Fresh biomass and root weight of the plants treated with (+) or without (-) NH$_3$ exposure, Exp 1.

Table 2. Leaf dry matter (DM) and nitrogen (N) concentration of plants treated with (+) or without (-) atmospheric ammonia (NH$_3$) exposure for 12 wks Exp 1.

Treatment		DM (%)			N (%)		
		Wk 0	Wk 6	Wk 12	Wk 0	Wk 6	Wk12
NH$_3$:	(-)	27.1	30.8	36.6	3.84	3.67^{b}	3.51^{b}
	(+)	26.9	43.0	47.9	3.82	6.44^{a}	7.05^{a}
Species:							
	R	46.9^{a}	70.9^{a}	64.2^{a}	1.63^{c}	1.95^{c}	2.26^{c}
	L	26.9^{b}	25.8^{b}	32.8^{bc}	4.92^{a}	7.46^{a}	7.15^{a}
	P	19.1^{c}	28.9^{b}	51.0^{ab}	5.35^{a}	6.81^{a}	7.12^{a}
	G	15.1^{c}	22.1^{b}	21.0^{c}	3.41^{b}	4.00^{b}	4.61^{b}
NH$_3$ x Species:							
	(-) × R	47.5	57.6	64.8	1.53	1.57^{d}	1.84^{e}
	(-) × L	26.8	25.1	31.9	4.88	5.49^{b}	5.32^{bc}
	(-) × P	18.8	18.9	30.3	5.49	4.55^{b}	4.04^{cd}
	(-) × G	15.2	21.7	19.5	3.45	3.08^{c}	2.86^{de}
	(+) × R	46.2	84.1	63.5	1.74	2.34^{cd}	2.68^{de}
	(+) × L	27.1	26.5	33.8	5.00	9.44^{a}	8.99^{a}
	(+) × P	19.3	38.9	71.7	5.20	9.07^{a}	10.20^{a}
	(+) × G	15.0	22.6	22.5	3.37	4.91^{b}	6.36^{b}
Sources of Variances:		---------------------------------- Probabilities --------------------------------					
NH$_3$		0.93	0.09	0.07	0.87	0.02	0.0001
Species		0.0001	0.0001	0.0002	0.0001	0.0001	0.0001
NH$_3$ × Species		0.92	0.07	0.06	0.61	0.0001	0.0001

[a-e] Means in a column with no common superscripts differ significantly ($P \leq 0.05$).



	6 week	12 week	6 week	12 week	6 week	12 week
	Honey locust		Hybrid poplar		Reed canary grass	
☐ (-) NH3	1.38	1.7	0.86	1.22	0.67	0.56
■ (+) NH3	2.63	3.04	3.53	7.31	1.12	1.43

Figure 2. Total foliage N of the plants at 6 and 12 wk treated with (+) or without (-) NH_3 exposure (fresh leaf wt before and after NH_3 exposure at 6 wk were 8.95 and 9.0 g for locust, 10.88 and 9.33 g for poplar, and 9.93 and 13.6 g for grass, respectively; while at 12 wk they were 14.85 and 24.68 g for locust, 4.68 and 3.85 g for poplar, and 14.07 and 13.8 g for grass, respectively), Exp 1.

There was a numerical trend for NH_3 exposure to increase leaf color scores at week 6 (P=0.10) and 12 (P=0.09) and mean leaf damage scores at week 6 (P=0.06) and 12 (P= 0.09) (Table 3). There were also highly species-dependent responses to NH_3 as shown by higher leaf color and damage scores. This indicated that some species were sensitive to NH_3, e.g. cedar, poplar, and grass whereas the locust color was enhanced by NH_3 treatment and showed lower damage values than other species.

Experiment 2

The greater plant foliar N resulting from NH_3 exposure was apparent at 6 wk compared with non-exposed plants (4.99 vs. 2.83%; $P \leq 0.05$) (Table 4). A similar trend in foliar DM was also observed with NH_3 exposure (57.4 vs. 46.5%; P=0.16). Poplar and willow deposited more N in their leaves than the other two species (arbovitae and spruce). Although the probability value did not indicate a significant NH_3 by species interaction on foliar N of the plants at 6 wk, the numerical trend toward greater foliar N in those exposed to NH_3 was discernable, particularly in arborvitae, poplar, and willow (P=0.13). This was also supported by a numerical trend of foliar DM at the same period.

Higher average leaf color scores and leaf damage scores due to NH_3 exposure was also observed e.g. 3.48 vs. 3.08 (P=0.14) and 4.51 vs. 4.40 (P=0.74), respectively (Table 5). Different plant species showed different responses to NH_3 exposure with poplar and willow showing greater leaf color and damage scores than arborvitae and spruce. However, there were no NH_3 by species interactions observed for plant color and damage scores.

Table 3. Leaf color and damage scores of plants treated with (+) or without (a) ammonia (NH$_3$) exposure for 12 wk, Exp 1.

Treatments	Color Score			Damage Score		
	Wk 0^{1}	Wk 6	Wk 12	Wk 0^{1}	Wk 6	Wk 12
NH$_3$: (-)	2.21	2.12	2.86	1	2.60	4.42
(+)	2.21	2.50	3.22	1	4.05	5.40
Species (Spec):						
R	2.00	2.78^{a}	3.86^{a}	1	3.15^{b}	5.59^{a}
L	3.00	1.39^{c}	1.75^{b}	1	1.54^{c}	3.90^{b}
P	2.00	2.88^{a}	4.32^{a}	1	4.42^{a}	6.08^{a}
G	2.00	2.18^{b}	2.25^{b}	1	4.18^{ab}	4.07^{b}
Fertilizer (Fert):						
(+)	2.21	2.31	2.96	1	3.46	4.78
(-)	2.21	2.31	3.13	1	3.18	5.04
Spec x Fert:	…^{2}	…	…	-	…	…
NH$_3$ x Spec:						
(-) × R	-	2.57^{ab}	3.90^{ab}	-	2.96^{b}	5.11^{abc}
(-) × L	-	1.62^{bc}	2.17^{cd}	-	1.20^{c}	4.54^{bcd}
(-) × P	-	2.44^{ab}	3.77^{ab}	-	2.55^{b}	5.17^{abc}
(-) × G	-	1.85^{bc}	1.62^{cd}	-	3.69^{b}	2.85^{d}
(+) × R	-	2.98^{a}	3.82^{ab}	-	3.35^{b}	6.06^{ab}
(+) × L	-	1.16^{c}	1.33^{d}	-	1.88^{c}	3.25^{cd}
(+) × P	-	3.31^{a}	4.87^{a}	-	6.28^{a}	6.99^{a}
(+) × G	-	2.51^{ab}	2.87^{bc}	-	4.68^{ab}	5.28^{abc}
NH$_3$ × Fert:	…	…	…	…	…	…
NH$_3$ × Spec × Fert	…	…	…	…	…	…
Sources of Variances:			Probabilities			
NH$_3$	-	0.10	0.09	-	0.06	0.09
Spec	-	0.0001	0.0001	-	0.0001	0.0001
Fert	-	0.97	0.43	-	0.38	0.44
Spec × Fert	-	0.44	0.13	-	0.92	0.20
NH$_3$ × Spec	-	0.03	0.002	-	0.001	0.001
NH$_3$ × Fert	-	0.33	0.27	-	0.16	0.06
NH$_3$ × Spec × Fert	-	0.19	0.08	-	0.75	0.06

[a-d] Means in a column with no common superscripts differ significantly ($P \leq 0.05$).

[1] Data at week 0 were not subjected to ANOVA because there were no differences within each species.

[2] Mean values are not shown because they did not have significant probabilities ($P \geq 0.05$).

Table 4. Leaf dry matter (DM) and nitrogen (N) concentration of plants treated with (+) or without (-) atmospheric ammonia (NH_3) exposure for 6 wk, Exp 2.

Treatment	DM (%)		N (%)	
	Wk 0	Wk 6	Wk 0	Wk 6
NH_3: (-)	29.9	46.5	2.62	2.83[a]
(+)	30.9	57.4	2.67	4.99[b]
Species:				
Arbovitae (A)	41.2[a]	37.9[b]	1.75[c]	3.12[b]
Poplar (P)	22.8[c]	77.1[a]	3.35[b]	4.86[a]
Spruce (S)	33.5[b]	39.5[b]	1.45[c]	2.10[b]
Willow (W)	24.2[c]	53.3[b]	4.04[a]	5.55[a]
NH_3 × Species:				
(-) × A	39.7	34.5	1.67[c]	2.24
(-) × P	22.9	79.3	3.54[ab]	3.55
(-) × S	33.3	37.3	1.49[c]	1.55
(-) × W	23.8	35.0	3.78[ab]	3.96
(+) × A	42.7	41.3	1.83[c]	4.00
(+) × P	22.7	75.0	3.15[b]	6.17
(+) × S	33.7	41.8	1.41[c]	2.65
(+) × W	24.6	71.5	4.29[a]	7.14
Source of Variances:	Probabilities			
NH_3	0.36	0.16	0.77	0.04
Species	0.0001	0.0001	0.0001	0.0001
NH_3 × Species	0.71	0.09	0.05	0.13

[a-c] Means in a column with no common superscripts differ significantly ($P \leq 0.05$).

Table 5. Leaf color and damage scores of plants treated with (+) or without (-) ammonia (NH_3) exposure for 6 wk, Exp 2.

Treatment		Color Score		Damage Score	
		Wk 0[1]	Wk 6	Wk 0[1]	Wk 6
NH_3:	(-)	2.02	3.08	1	4.40
	(+)	2.00	3.48	1	4.51
Species:					
A		2.00	1.61^d	1	1.56^b
P		2.00	4.88^a	1	6.96^a
S		2.00	2.57^c	1	2.29^b
W		2.03	4.04^b	1	7.00^a
NH_3 x Species:					
	(-) × A	2.00	1.50	1	1.40
	(-) × P	2.00	4.92	1	6.92
	(-) × S	2.00	2.54	1	2.27
	(-) × W	2.00	3.33	1	7.00
	(+) × A	2.00	1.73	1	1.73
	(+) × P	2.00	4.85	1	7.00
	(+) × S	2.00	2.60	1	2.30
	(+) × W	2.00	4.75	1	7.00
Source of Variances:		---------------------------------- Probabilities ----------------------------------			
NH_3		-	0.14	-	0.74
Species		-	0.0001	-	0.0001
NH_3 × Species		-	0.12	-	0.98

[a-c]Means in a column with no common superscripts differ significantly ($P \leq 0.05$).

[1] Data at week 0 were not subjected to ANOVA because there were no differences within each species.

Discussion

The superior growth of locust (Exp 1) compared with other species is likely due to the unique symbioses of its roots with bacteria in fixating air NH_y (Zahran, 2001). Because the effect of fertilizer on plant heights at wk 6 did not show any impact within a species, this suggested that growth response of plants to fertilizer was unique to each species. Visual observation of red cedar in the (+) NH_3 chambers in Exp 1 showed that new shoots became dry as they emerged indicating metabolic disturbance or necrosis, which was possibly due to NH_3 exposure. The same symptoms occurred in Exp 2 with the spruce. Krupa (2003) reported that needle necrosis following needle drying was a common response of conifers to NH_3 near livestock farms. These species will become very sensitive when they are exposed to NH_3 for long periods of time (Van deer Eerden, 1982).

The greater leaf N of honey locust, hybrid poplar, and grass observed in Exp 1 and the numerical trend in Exp 2 indicated greater metabolism or detoxification of the absorbed NH_3-N (Fangmeier et al., 1994). However, greater N deposition in leaves does not necessarily mean that all the plants, especially hybrid poplar (Exp 1 and 2), grass (Exp 1), willow, and spruce (Exp 2) benefited from continuous atmospheric NH_3 exposure in a closed chamber as shown by the poor leaf color quality and damaged leaves (Tables 3 and 5). Exposure to 4 to 5 ppm of NH_3 under a 16L:8D photoperiod was seemingly sufficient to elicit the adverse effects of NH_3 on these species. Black spots and necrosis indicated by leaf-tip drying were the two consistent symptoms of foliar tissues in the current experiments and consistent with the other findings as reviewed by Krupa (2003). Visual injury of the plant foliage is associated with NH_3 exposure and increased arginine levels have been reported with yellowing of young needles in *Pinus sylvestris* (Roelofs, 1987a, 1987b). This type of injury was clearly seen among red cedar in Exp 1, spruce, and some arborvitae in Exp 2 in the (+) NH_3 chambers. Visible injury in honey locust did not seem to be as great as in other species supporting the fact that this species might have benefited from NH_3 exposure as also indicated by its superior growth.

It is important to note that Two-Spotted Spider Mites were in evidence among the locust, poplar, and cedar from week 6 on in the (+) NH_3 chambers in Exp 1, although all the plants were sprayed with a miticide at the start of the experiment and again at 3 and 6 wk. The presence of these mites might have contributed to leaf color and damage scores of the plants since one of the contributing effects of elevated leaf N due to NH_3 exposure is increased sensitivity to insect pest infestation (Krupa, 2003). Therefore, it was not surprisingly to find numerically greater damage scores of all plants in the (+) NH_3 chamber compared to those in the (-) NH_3 chambers at 6 and 12 wk in Exp 1 (Table 3).

Overall, this study demonstrated that plant foliage has the potential to absorb NH_3-N discharged from the exhaust fans of poultry and livestock barns. As an example, assume the average concentration of NH_3 in a small hen house (4,000 birds) with four 61-cm exhaust fans is 30 ppm (Wathes et al., 2003; Miles et al., 2004) (equivalent to 0.020833 g m^{-3} [Krupa, 2003]), and each of the four 61-cm fans is discharging 140,213 m^3 of air d^{-1}, and if approximately 30% of NH_3-N is trapped by the plant foliage; then the foliar biomass required to trap this amount of NH_3-N will be 47 to 108 kg d^{-1} of poplar, 215 to 231 kg d^{-1} of locust, or 331 to 665 kg d^{-1} of grass based on the data herein. With this knowledge one can calculate the foliar biomass and number of trees or grasses to plant around a commercial poultry house to reduce ammonia emissions and environmental pollution.

Conclusions

Foliar condition and nutrient concentration appeared to be the more sensitive plant indicators of continuous anhydrous NH_3 exposure in environmentally controlled chambers. Although almost all the species deposited more N in their leaves due to NH_3 exposure, only honey locust appeared to tolerate and might have benefited from the continuous 4 to 5 ppm NH_3 exposure.

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References

Fangmeier, A., A. Hadwiger-Fangmeier, L. Van deer Eerden, and H.-J. Jäger. 1994. Effects of atmospheric ammonia on vegetation - a review. *Environmental Pollution* 86: 43-82.

Krupa, S.V. 2003. Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: a review. *Environmental Pollution* 124: 179-221.

Miles, D.M., S.L. Branton, and B.D. Lott, B.D. 2004. Atmospheric ammonia is detrimental to the performance of modern commercial broilers. *Poultry Science* 83: 1650-1654.

Patterson, P.H., and E.S. Lorenz, E.S. 1996. Manure nutrient production from commercial white leghorn hens. *Journal of Applied Poultry Research* 5: 260-268.

Patterson, P.H., and E.S. Lorenz, E.S. 1997. Nutrients in manure from commercial white leghorn pullets. *Journal of Applied Poultry Research* 6: 247-252.

Patterson, P.H., E.S. Lorenz, E.S., and W.D. Weaver, Jr. 1998. Litter production and nutrients from commercial broiler chickens. *Journal of Applied Poultry Research* 7: 247-252.

Patterson, P.H., R.M. Hulet, R.M., and E.S. Lorenz, E.S. 1999. Litter production and nutrients from commercial turkeys. The Pennsylvania State University, State College, PA 16802, USA. Unpublished data.

Pitcairn, C.E.R., I.D. Leith, L.J. Sheppard, M.A. Sutton, D. Fowler, R.C. Munro, S. Tang, and D. Wilson. 1998. The relationship between nitrogen deposition, species composition, and foliar nitrogen concentrations in woodland flora in the vicinity of livestock farms. *Environmental Pollution* 102(S1): 41-48.

Roelofs, J.G.M., A.W. Boxman, and H.F.G. Van Dijk. 1987a. Effects of airborne ammonium on natural vegetation and forests. Pages: 266-276 In: *Ammonia and Acidification Symposium*, EURASAP (13-15 April, 1987). Asman, W.A.H., and H.S.M.A Diederen, Eds. RIVM/TNO Bilthoven, The Netherlands.

Roelofs, J.G.M., A.W. Boxman, and H.F.G. Van Dijk. 1987b. Effects of airborne ammonium on natural vegetation. Pages: 876-880 In: *Air Pollution and Ecosystems, Proceeding International Symposium*. (18-22 May, 1987). Mathy, P., Ed. Grenoble, France.

SAS Institute. 1999. *SAS User's Guide: Statistics*. Version 8 ed. SAS Institute, Inc. Cary, NC.

Seedorf, J., and J. Hartung. 2000. Emission of airborne particulates from animal production. In: *2000-Livestock Farming and the Environment Workshop Series of Conference: Section of Sustainable Animal Production*. http://www.agriculture.de/acms1/conf6/ws4dust.htm (August, 2005).

Van deer Eerden, L.J.M. 1982. Toxicity of ammonia to plants. *Agriculture and Environment* 7: 223-235.

Van deer Eerden, L.J.M., W. De Vries, and H. Van Dobben. 1998. Effects of ammonia deposition on forests in the Netherlands. *Atmospheric Environment* 32:525-532.

Wathes, C.M., T.G.M. Demmers, and H. Xin. 2003. Ammonia concentrations and emissions in livestock production facilities: guidelines and limits in the USA and UK. Paper No. 034112 In: *ASAE Annual International Meeting* (July 27-30, 2003, Las Vegas, Nevada). The ASAE, St. Joseph, MI, USA.

Yin, Z.-H., W. Kaiser, U. Heber, U., and J.A. Raven, J.A. 1998. Effects of gaseous ammonia on intracellular pH values in leaves of C_3- and C_4-plants. *Atmospheric Environment* 32:539-544.

Zahran, H.H. 2001. Rhizobia from wild legumes: diversity, taxonomy, ecology, nitrogen fixation, and biotechnology. *Journal of Biotechnology* 91:143-153.

Plant Foliar Nitrogen and Temperature on Commercial Poultry Farms in Pennsylvania

P.H. Patterson[1], Adrizal[1], R.M. Hulet[1], R.M. Bates[2], C.A.B. Myers[3], G.P. Martin[4], R. Shockey[5], and M. van der Grinten[6],
[1]Department of Poultry Science, [2]Department of Horticulture, [3]Berks County Cooperative. Extension, [4]Lancaster County Cooperative. Extension, Penn State University, University Park, PA 16802,
[5]United States Department of Agriculture (USDA) National Resources Conservation Service (NRCS), Harrisburg, PA 17110,
[6]USDA-NRCS-Big Flats Plant Materials Center, Corning, NY 14830.

Abstract

Trees have been planted for many years in agriculture settings for windbreaks and shade purposes. A new, but largely untested benefit may be as a visual screen for combating neighbor issues, as a barrier for flies, and as a filter for fan emissions from poultry and livestock farms. This field study sought to evaluate the potential of trees planted around commercial poultry farms to trap NH_3, the gas of greatest environmental concern to the poultry industry. Four plant species (spruce, poplar, streamco willow, and hybrid willow) were planted in front of the exhaust fans of eight commercial farms from 2003 to 2004. In 2005 because temperature (T) can be a stressor for trees, T was monitored with data loggers among the trees in front of the exhaust fans (11.4 m to 17.7 m) and at a control distance away from the fans (≥48 m) during all four seasons in Pennsylvania. Poplar and spruce foliage samples were taken in August 2005 from one turkey and two layer farms for dry matter (DM) and nitrogen (N) analysis. The two layer farms had poplar plantings and all three farms had spruce. The results showed that farm type had a significant effect on plant leaf DM but not leaf N. Although poplar had less foliage DM compared to spruce (41.3 vs. 50.1%), it contained greater N (3.43 vs. 2.46%). Plant location clearly showed greater foliar DM and N levels among those plants near the fans compared with controls, 51.0 vs. 40.4% and 3.61 vs. 2.28%, respectively. Greater foliar DM may have resulted from the plants' capacity to trap NH_3-N emitted by the exhaust fans resulting in better N status in the tissues, growth and biomass of the plant, or desiccation of the plants from the proximity of the fans. However, the difference in foliar DM and N concentrations due to species, location, and the interaction of the two factors was unlikely correlate with ambient T. Summer T were similar in front of the fans and at a control distance away from the fans on all farms (25.80 vs. 25.32C-layer 1, 25.92 vs. 25.53C-layer 2, and 25.45 vs. 25.54C-turkey) suggesting no greater T stress associated with fan proximity.

Introduction

Air emissions from poultry and livestock production are numerous and may include dust or particulate matter, odors and nitrogenous compounds including ammonia. Ammonia (NH_3) emissions can be significant. Our own data using mass balance techniques on commercial pullet, laying hen, broiler and turkey farms indicates that between 18 to 40% of feed N is lost to the atmosphere mostly as NH_3-N (Patterson and Lorenz, 1996, 1997; Patterson et al. 1998, Patterson et al., 1999). Planting trees around poultry farms has been utilized for wind breaks and for shade. Recently vegetative shelterbelts have been used as a visual screen, a barrier for fly migration and to trap emissions (odors, dust, and gases) discharged by the exhaust fans from poultry farms (Malone, 2004).

Plants have the capacity to absorb aerial ammonia (NH_3) via foliar stomata and cellular assimilation through the glutamine synthetase and glutamate synthase pathways (Yin et al., 1998). Van deer Eerden et al. (1998) reported that at the right concentrations, NH_y ($NH_3 + NH_4^+$) would favor plant growth, but at a critical threshold it would cause tissue necrosis, reduced growth, and greater frost sensitivity.

In chamber studies we determined that multiple plant species including red cedar, white spruce, arbovitae, honey locust, hybrid poplar, streamco willow, and reed canary grass deposited almost two-fold greater N in their leaves when exposed to continuous NH_3 at 4 to 8 ppm, compared to control chambers without atmospheric NH_3 (Adrizal et al., 2006). However, only honey locust consistently grew well and showed little foliar injury compared to other species; indicating its capacity to tolerate and utilize aerial NH_3-N.

Malone (2004) planted three plant species (4.9 m high bald cypress, 4.3 m high Leyland cypress, and 2.4 m high red cedar, 9m wide) at 9, 12.2, and 14.6 m downwind of the tunnel fans on a roaster chicken farm. During the summer, the trees reduced air velocity by 99%, dust by 50-53%, and NH_3 by 29-67% down wind of the trees. One concern faced by extension personnel sighting trees for poultry farms was that heat exhausted from the poultry barns in winter may throw plant species out of dormancy, or result in temperature and/or dehydration stress on the plants. This study was designed to evaluate the potential of trees planted around poultry house exhaust fans to trap NH_3, and the impact of tree proximity to the fans on environmental temperature and its associated stressors.

Materials and Methods

There were eight commercial poultry farms involved in this study including 3 broiler, 3 layer, 1 pullet, and 1 turkey farm. Cox tracer data loggers (Model CT-1E-D-16, Sensitech, Inc. MA, USA) were used to monitor temperature (T) on all farms at two locations. The first T logger was placed away from the buildings and fans (≥48 m, control), while the second was placed near the fans (11.4 to 17.7m) among the trees. Each logger was hung inside the wall of a propylene shield and secured horizontally to a metal post at 1.5 m high from the ground matching the height of the facing fan. All the loggers were programmed to record the T every 30 min continuously for two consecutive months in each season (winter: January to February; spring: April to May; summer: July to August; fall: October to November) in 2005.

More than 2000 plants (Norway spruce [*Picea abies*], hybrid willow [*Populus sp.*], and streamco willow [*Salix purpurea*]) were planted in rows on the all poultry farms from 2003 to 2004 (Table 1). In 2005, monitoring for T began in August, and foliage samples from three plants of each species were taken from the selected farms based on row position and distance from the exhaust fans.

Table 1. Characteristics of commercial poultry farms and trees.

Farm	House type	Birds & houses	Farm issues	Trees
Broiler 1	litter	21,000/house	Visual screen, snow load, odors and dust	2 rows Norway spruce 1 row hybrid willow 1 row streamco willow
Broiler 2	litter	50,000/2 houses	Dust , odors and snow load	1 row Norway spruce 1 row hybrid willow 1 row streamco willow
Broiler 3	litter	20,000/house	Dust and odors	1 row streamco willow
Layer 1	high-rise	125,000/house	Dust, odors, flies and visual screen	2 rows Norway spruce 2 rows hybrid poplar
Layer 2	high-rise	475,000/3 houses	Dust, odors and flies	2 rows Norway spruce 1 row hybrid poplar 1 row streamco willow
Layer 3	high-rise	1,000,000/8 houses	Visual screen, dust and odors	2 rows Norway spruce
Pullet	high-rise	83,000/house	Visual screen, snow load, energy conservation, and urban encroachment	2 rows Norway spruce 1 row hybrid willow
Turkey	litter	40,000/2 houses	Dust, odors, water quality, feathers and truck traffic	2 rows hybrid willow 10 rows Norway spruce

An incomplete randomized block design was applied in this study where farms were considered as a block. The two mathematical models employed were Model 1 for the analysis of T and Model 2 for the analysis of foliar DM and N data using Proc GLM of SAS followed by Bonferroni test for plant significance (SAS Institute, 1999). The foliar percentage DM and N data were transformed to arc sin before the analysis. The two models are described below:

$$X_{ijk} = \mu + F_i + L_j + \varepsilon_{ijk} \qquad \text{….. (Model 1)}$$
$$X_{ijkl} = \mu + F_i + S_j + L_k + (S\times L)_{jk} + \varepsilon_{ijkl} \qquad \text{….. (Model 2)}$$

where X_{ijk} is the observed value, μ is the overall mean, F_i is the i-th farm, L_j is the j-th location where the temperature was monitored (Model 1), S_j is the j-th plant species, L_k is the k-th location where the plants were planted (Model 2). $(S\times L)_{jk}$ is the species by location effect at j- and k-th combination, and ε_{ijk} or ε_{ijkl} is the residual errors for Model 1 and Model 2, respectively.

Results

Farm type had a significant effect on plant foliar DM ($P\leq 0.001$) but not on foliar N concentration (Table 2). The average DM concentrations of plants from the two layer farms were greater than that from the turkey farm.

Plant species and location showed significant effects on both foliar parameters (Table 2). Poplar was found to have less DM in its leaves than spruce (41.3 vs. 50.1%; $P\leq 0.05$), but greater foliar N levels (3.43 vs. 2.46%; $P\leq 0.05$). Planting location clearly showed greater foliar DM and N levels in those plants located near the exhaust fans compared with controls with 51.0 vs. 40.4% DM and 3.61 vs. 2.28% N, respectively. There was a significant species by location interaction with greater tissue DM again near the fans in both species, and a similar trend with tissue N levels, although not significantly so.

Table 2. Foliar DM and N (%) of hybrid polar (*Populus sp*) and Norway spruce (*Picea abies*) sampled at commercial poultry farms.

	DM (%)	N (%, DM)
Farm:		
Layer 1	47.2^{a}	3.16
Layer 2	53.7^{a}	2.91
Turkey	36.3^{b}	2.77
Species:		
Poplar	41.3^{b}	3.43^{a}
Spruce	50.1^{a}	2.46^{b}
Location:		
Control	40.4^{b}	2.28^{b}
Fan	51.0^{a}	3.61^{a}
Species × Location		
Poplar × Control	31.9^{b}	2.68
Poplar × Fan	50.6^{a}	4.19
Spruce × Control	48.8^{a}	1.88
Spruce × Fan	51.4^{a}	3.03
SEM	4.4	0.34
Sources of variances:	--------------Probabilities	---------------
Farm	0.001	0.484
Species	0.008	0.001
Location	0.001	0.0001
Species × Location	0.009	0.696

$^{a\text{-}b}$Means in a column with no common superscripts differ significantly ($P\leq 0.05$).

The temperature data presented in Table 3 showed that none of the factors (farm type or location) had an impact on the temperatures recorded throughout all four seasons ($P > 0.05$). However, temperature differences were realized in all seasons and followed the same pattern on all farms, ranging from -0.06 to 1.22 °C in winter, 13.56 to 16.96 °C in spring, 24.71 to 28.06 °C in summer, and 9.28 to 12.56 °C in fall

(Table 3). Summer T's were similar near the fans and at the control distance away from the fans on all three farms where plant tissues were sampled (25.80 vs. 25.32 °C [layer 1], 25.92 vs. 25.53 °C [layer 2], and 25.45 vs. 25.54 °C [turkey]). This indicated temperature stress was not an issue for trees near the fans.

Table 3. Average temperature recorded at two locations (control vs. downwind of the exhaust fans) on commercial poultry farms during the four seasons of 2005.

Farms	Winter		Spring		Summer		Fall	
(initial)	Control	Fan	Control	Fan	Control	Fan	Control	Fan
	-------------------------	-------------------------	-------------------------	------------------------- (ºC)[1]	-------------------------	-------------------------	-------------------------	-------------------------
Broiler 1	0.26±7.14	0.28±7.08	14.68±7.78	14.10±7.02	28.06±7.53	27.33±7.10	10.57±7.41	12.56±8.75
Broiler 2	1.22±6.55	0.60±6.07	16.69±6.37	16.9±56.40	26.20±6.03	26.81±6.41	9.85±7.29	9.89±7.17
Broiler 3	0.16±6.27	-0.27±5.84	16.57±6.99	16.96±7.24	25.24±6.21	25.79±5.89	10.70±7.48	11.40±7.66
Layer 1	-0.06±7.54	-0.67±6.94	15.41±5.81	15.37±6.24	25.32±6.11	25.80±6.56	9.66±7.13	9.28±7.46
Layer 2	-1.20±6.50	-0.22±7.06	13.78±7.15	[2]	25.53±6.18	25.92±5.55	9.44±7.18	10.16±7.30
Layer 3	0.11±4.80	0.30±4.80	15.51±7.42	16.24±7.36	24.97±6.75	24.90±5.61	9.34±7.37	9.42±7.42
Pullet	1.38±5.11	0.99±4.95	15.96±7.54	16.74±6.24	25.51±6.90	24.71±6.47	9.79±7.57	9.50±7.31
Turkey	-2.08±6.79	-0.26±8.82	[2]	13.56±8.43	25.54±7.45	25.45±6.72	11.00±8.17	[2]

[1] Data (means ± SD) were recorded with data loggers programmed to read the temperature every 30 min for two months per season (winter: January to February; spring: April to May; summer: July to August; and fall: October to November).

[2] Technical failure of the data loggers resulted in no temperatures recorded at these locations.

Discussion

Ammonia concentration at the trees located near the exhaust fans was not measured in the current study. However, previous studies have documented ammonia losses from poultry farms (Liang et al., 2005; Miles et al., 2006; Patterson and Lorenz, 1996, 1997, Patterson et al., 1998; Patterson et al., 1999). Recently, Adrizal et al., (2006) demonstrated that plants grown in environmental chambers with atmospheric ammonia at 4 to 7ppm deposited almost 2-fold more N in their leaves compared to control plants in chambers without ammonia. Significantly great tissue DM was also observed in these studies, much like what was documented on the poultry farms herein. Although, not all plant species appeared to benefit from the ammonia exposure in the chamber studies. Hybrid poplar was the species with the greatest capacity to incorporate atmospheric ammonia into foliar tissue. However, the poplar also had the greatest tissue damage and negative color scores compared to the other species, suggesting upper limits to ammonia tolerance. The tissue injuries observed on the plants exposed to NH_3 in environmentally controlled chambers, however, were not apparent among plants on the poultry farms in the current field study. This suggests greater plant tolerance to NH_3 exposure under outdoor conditions that may included rain cleansing, and lower ammonia concentrations.

Reduced air velocity, dust, and NH_3 levels have been reported by Malone (2004) downwind of trees planted in front of poultry fans. Pitcairn et al. (1998) documented fewer numbers of nitrophilus plant species at distances downwind of the fans on livestock farms. Each of these demonstrates the importance of planting distance for the capacity of plant tissues to trap aerial NH_3-N emitted by the exhaust fans, and the sensitivity of some species. Lastly, temperature results from this study demonstrated that exhausted air temperature from buildings housing commercial poultry are not a plant stressor or affect the dormancy cycle of the trees planted within 11 to 18m from the fans.

Conclusions

Environmental temperatures monitored near commercial poultry house fans (11.4 to 17.7 m) did not differ from those at control distances from the fans (≥48 m) during all four seasons in Pennsylvania. Hybrid poplar and Norway spruce foliar N and DM concentrations were greater in the foliage sampled near the fans compared to the controls plants. Under the conditions of this study, both hybrid poplar and Norway spruce were able to trap aerial NH_3-N emissions from the fans and tolerate the concentration of ammonia realized under these field conditions.

References

Adrizal, P.H. Patterson, R.M. Hulet, and R.M. Bates. 2006. Growth and foliar nitrogen status of four plant species exposed to atmospheric ammonia. *Journal Environmental Science and Health-Part B*. 41: (accepted).

Liang, Y., H. Xin, E.F. Wheeler, R.S. Gates, H. Li, J.S. Zajaczkowski, P. Topper, K.D. Casey, B.R. Behrends, D.J. Burnham, and F.J. Zajaczkowski. 2005. Ammonia emissions from U.S. laying hen houses in Iowa and Pennsylvania. *Transactions of the ASAE* 48: 1927-1941.

Malone, B. 2004. Using trees to reduce dust and odor emissions from poultry farms. Pages: 33-38 In: *Proceedings of Poultry Information Exchange* (April 19, 2004). Sufers Paradise, Queensland, Australia.

Miles, D.M., P.R. Owens, and D.E. Rowe. 2006. Spatial variability of litter gaseous flux within a commercial broiler house: ammonia, nitrous oxide, carbon dioxide, and methane. *Poultry Science* 85: 167-172.

Patterson, P.H. and E.S. Lorenz. 1996. Manure nutrient production from commercial White Leghorn hens. *Journal Applied Poultry Research* 5: 260-268.

Patterson, P.H. and E.S. Lorenz. 1997. Nutrients in manure from commercial White Leghorn pullets. *Journal Applied Poultry Research* 6: 247-252.

Patterson, P.H., E.S. Lorenz, and W.D. Weaver, Jr. 1998. Litter production and nutrients from commercial broiler chickens. *Journal Applied Poultry Research* 7: 247-252.

Patterson, P.H., R. M. Hulet and E.S. Lorenz. 1999. Litter production and nutrients from commercial turkeys. The Pennsylvania State University, University Park, PA. Unpublished data.

Pitcairn, C.E.R., I.D. Leith, L.J. Sheppard, M.A. Sutton, D. Fowler, R.C. Munro, S. Tang, and D. Wilson. 1998. The relationship between nitrogen deposition, species composition, and foliar nitrogen concentrations in woodland flora in the vicinity of livestock farms. *Environmental Pollution* 102(S1): 41-48.

SAS Institute. 1999. *SAS User's Guide: Statistics*. Version 8 ed. SAS Institute, Inc. Cary, NC.

Van deer Eerden, L.J.M., W. De Vries, and H. Van Dobben. 1998. Effects of ammonia deposition on forests in the Netherlands. *Atmospheric Environment* 32: 525-532.

Yin, Z.-H., W. Kaiser, U. Heber, U., and J.A. Raven, J.A. 1998. Effects of gaseous ammonia on intracellular pH values in leaves of C_3- and C_4-plants. *Atmospheric Environment* 32: 539-544.

An Assessment of the Role of Terrain and Land Cover in the Development of Local Wind Flow Patterns: Development and Validation of the Land Use/Land Cover Dataset

Joseph G. Alfieri[1], Dev Niyogi[1,2], Margaret A. LeMone[3], Fei Chen[3], Souleymane Fall[1]
[1]Department of Agronomy, Purdue University, West Lafayette, Indiana 47906
[2]Department of Earth and Atmospheric Sciences, Purdue University,
West Lafayette, Indiana 47906
[3]National Center for Atmospheric Science, Boulder, Colorado 80307

Abstract

Surface characteristics, such as terrain and Land Use/Land Cover (LULC) type, impose an important control on the land-atmosphere exchange processes leading to local wind flow patterns. In turn, these local wind flow patterns have a strong influence on the dispersion, distribution and deposition of atmospheric pollutants. As a result, a thorough understand of the role of the land surface in driving local wind flow patterns is necessary in order to accurately model the movement of these pollutants and assess air quality. In order to investigate the impacts of the land surface on these processes it is first necessary to develop am accurate LULC dataset. This research focused on the Walnut River Watershed (WRW) located in the Southern Great Plains (SGP) of the United States, a region that has been shown to be strongly affected by ozone, NO_x, and other pollutants. Specifically, this research compared two high-resolution (30 m) LULC datasets: the 1992 National Land Cover Dataset (NLCD 92) and the Kansas Gap Analysis Program dataset (GAP). While the two datasets agreed for the majority of the land area of the watershed, important differences due to classification and smoothing errors are evident. For example, small clusters of trees within riparian zones are often omitted from the LULC datasets. The differences resulted in an uncertain or inaccurate classification of approximately 27% of the total area of the WRW (Figure 1). Moreover, neither dataset achieved an overall accuracy of 80% with the NLCD 92 dataset having an overall accuracy of 68.7% and the GAP dataset having an overall accuracy of 79.2% within the WRW. Relationships between LULC type and surface characteristics, such as the normalized difference vegetation index (NDVI) and elevation, were developed using only those pixels where both LULC datasets agreed. For example, a strong relationship was found between LULC type and elevation. Using a reallocation scheme based on these relationships, the uncertain pixels within the WRW were reclassified. The resulting map (Figure 2) had on overall accuracy approaching 93%, more 24% greater than the NLCD 92 dataset and nearly 14% greater than the GAP dataset. In particular, the revised LULC dataset demonstrated an improved representation of Open Water, Wetland, and Wooded LULC types. For example, the User's Accuracy of the Wooded LULC type increased by more than 25% from approximately 71% in the case of either the NLCD 92 or GAP datasets to more than 96% in the case of the revised LULC dataset. This research represents

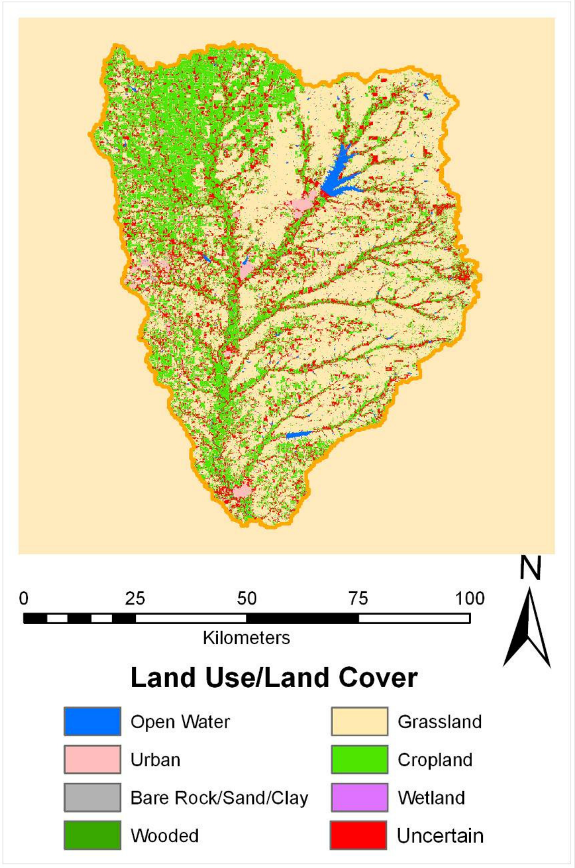

Figure 1. The LULC types within the WRW, as well as those areas with an uncertain classification, are shown.

an important first step toward understanding the influence of surface properties on both local wind flow patterns and the downwind transport and deposition of atmospheric pollutants. Future research will focus on the use of remote sensing and surface observations to quantify and analyze the wind flow patterns within the WRW and their relationship to heterogeneous surface characteristics.

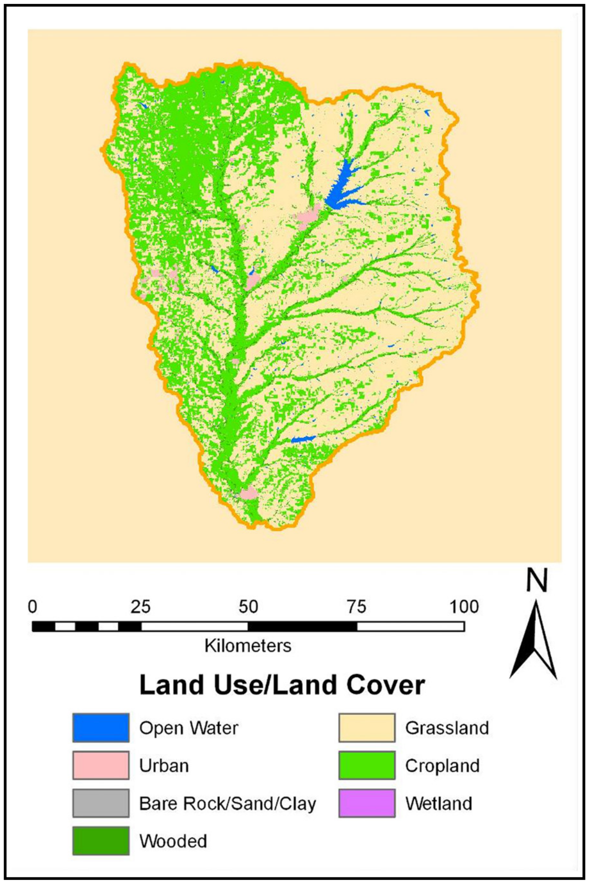

Figure 2. Using relationships between LULC distribution and surface characteristics, the revised LULC dataset shown was developed. It has an overall accuracy of 92.9%.

Dietary Modifications to Reduce Air Emissions from Broiler Chickens

R. Angel[1], W. Powers[2], S. Bastyr[2], W. Wu[2], and T. Applegate[3]
[1]University of Maryland, 4131 Animal Sciences Center, College Park, MD 20742, USA
[2]Iowa State University, 109 Kildee Hall, Ames, IA 50011, USA
[3]Purdue University, Lilly Hall of Life Sciences, West Lafayette, IN 47907, USA.

Abstract

The impact of feeding broilers reduced protein (LP) diets and control diets with industry protein and amino acid concentrations (C) on emissions of ammonia (NH_3), hydrogen sulfide (H_2S), nitric oxide (NO), nitrite (NO_2), carbon dioxide (CO_2), methane (CH_4) and non-CH_4 total hydrocarbon as well as on broiler performance and yields were determined. Broilers were housed in environmental chambers with continuously measured gas concentrations and airflows. Ross 308 male broilers were allocated to one of the chambers at hatch and grown for 42 days. Three sequential trials (flocks) were done to determine the impact of build-up litter. Broilers on the C treatment were fed based on a four phase feeding program: starter (St), grower (Gr), finisher (Fn), and withdrawal (Wd) diets. Broilers on the LP treatment were fed based on a six phase feeding program: prestarter (PreSt), St, Gr1, Gr2, Fn, and Wd diets. Formulated protein concentrations were 22.1, 20, 17.2, and 16.6% for the C St, Gr, Fn, and Wd diets, respectively while those for the LP PreSt, St, Gr1, Gr2, Fn, and Wd diets were 22.0, 18.6, 18.1, 17.3, 15.8, and 15%, respectively. Synthetic sources of lysine, methionine, isoleucine, valine, tryptophan, and argentine were used where needed to meet minimum requirements in the LP diets while only methionine and lysine were needed to in the formulation of the C diets. Body weight (BW) was determined by chamber at the start and end of each phase and feed disappearance (FC) determined at the end of each phase. Feed to gain ratio (FCR) was determined after correction for mortalities from the BW and FC data. Broilers on the C treatment weighed more at the end (42 days) over the three flocks (2.78 kg) than those on the LP treatment (2.69 kg) but FCR was similar (1.89 vs 1.91 for broilers fed C and LP treatments diets, respectively). Twenty broilers per chamber were randomly selected for yield determination in flock 3. Dress percent ((whole bird - gastrointestinal tract)/live weight) and breast yields (whole deboned breast weight/dress weight) was not affected by dietary treatment. Breast weight was also similar for both treatments (543 vs 541 g for broilers fed the C and LP treatment diets). Diet treatment affected NH_3 emissions in flock 1with the LP treatment resulting in lower daily NH_3 emissions (26.5 mg kg^{-1} in flock 1) compared to daily NH_3 emissions from broilers fed the C treatments diets (33.8 mg kg^{-1}). There was no effect of treatment on NO, NO_2, SO_2, H_2S, CO_2, CH_4, or non- CH_4 hydrocarbons in flock 1. Lowering dietary protein while maintaining minimum concentrations of amino acids resulted in substantial reductions in NH_3, NO, and NO_2 and no impact on breast weight or yield.

Introduction

Public and regulatory concerns related to air emissions from livestock and poultry operations has increased in recent years. Nuisance concerns with pollutants such as particulate matter, volatile organic compounds, ammonia (NH_3), methane, hydrogen sulfide, and odors have not subsided but there has been a refocused on human health implications. Outside of private lawsuits, state and federal regulatory agencies are seriously focusing on further determination of emissions to see if they fit current regulations or to determine if new regulations should be drafted. Of concern is the paucity of data on emissions from different livestock and poultry operations. An emission is the product of the concentration of the pollutant in question multiplied by a flow rate. Each of those factors has a unique set of measurement challenges associated with precision as well as methodology selection, that in most cases, still need to be resolved. In the absence of data, the regulatory community often will utilize the only information available – which can often produce less than adequate minimum standards. For example, regulatory agencies in California calculated poultry emissions based on emission factors for VOC from dairy cows. This was done under the misguided assumption that emissions should be same, for poultry and dairy, per unit of body weight (Mitloehner, 2005). Unfortunately, this is not the first time that policy preceded science, as we are entering an era where funding and timing of that funding relative to policy development does not go hand-in-hand.

Because there is very limited information in the published literature on the actual air emissions from broiler operations a study was done at a new air emissions chamber facility at Iowa State University to determine baseline air emissions of ammonia (NH_3), hydrogen sulfide (H_2S), nitric oxide (NO), nitrite (NO_2), carbon dioxide (CO_2), methane (CH_4) and non-CH_4 total hydrocarbon from broiler flocks grown on a "typical" industry phase feeding (control, C) and management program and on a reduced protein (LP) feeding program.

Materials and Methods

All animal procedures were approved by the institutional animal care committee. Ross 308 hatchling male broiler chickens were allocated to one of eight air emission chambers during each of three sequential 42-d flocks (50 chicks per chamber per flock). Chambers were randomly allocated at the start of each flock to one of two dietary treatment: a control treatment (C) that consisted of four feed phases: a 17-d starter (St, d 0 - 16), a 13-d grower (Gr, d 17 – 29), a 6-d finisher (Fn, d 30 - 35) and a 6-d withdrawal (Wd, d 36 – 42) and a reduced crude protein treatment (LP) that consisted of six feed phases: a 7-d pre-starter (PreSt, d 0 - 6), a 10-d starter (d 7 - 16), a 7-d grower 1 (Gr1, d 17 – 23), a grower 2 (Gr2, d 24 – 29), a 6-d finisher (d 30 - 35) and a 6-d withdrawal (d 36 – 41). Chamber body weight was measured and recorded at the start of each flock and on d 7, 17, 24, 30, 36, and 42. Feed disappearance was determined for each phase allowing for feed efficiency (feed to gain, FCR) calculations. Mortality was checked and recorded daily and feed efficiency was corrected for mortality. Diets were formulated to be isocaloric, by phase, were primarily corn and soybean based, but differed in protein content as follows: 22.1, 20, 17.2, and 16.6% for the C St, Gr, Fn, and Wd diets, respectively while those for the LP PreSt, St, Gr1, Gr2, Fn, and Wd diets were 22.0, 18.6, 18.1, 17.3, 15.8, and 15%, respectively. To maintain minimum amino acid (lysine, methionine, total sulfur amino acids, threonine, arginine, isoleucine, tryptophan, and valine) required concentrations in the diets synthetic amino acids were used. In C diets only synthetic lysine and methionine had to be used while in the LP diets lysine, methionine, threonine, arginine, tryptophan, valine and isoleucine were included in the diet. Diets were analyzed for dry matter, N, calcium (Ca), phosphorus (P), amino acids and selected microminerals.

At the end of flock 3, 20 broilers per chamber were randomly selected and sampled for yield determinations. Feed was removed 12 hours prior to sampling to ensure an empty body weight determination. Broilers were weighed individually, killed by cervical dislocation, the intestinal tract (from crop to cloaca) and abdominal fat pad removed for the determination of carcass weight. The breast was then removed and weighed. Clean wood shavings were sampled, placed in pans and weighed prior to the start of the first flock. Litter was weighed and sampled at the end of each flock for dry matter excretion determination as well as litter analysis (dry matter, nitrogen (N), calcium, phosphorus, and micromineral analysis) in order to provide estimates of volume and nutrient content excreted by broilers on each dietary treatment..

Throughout each flock, emissions of CO_2, NH_3, NO, NO_2, SO_2, H_2S, CH_4 and non-methane total hydrocarbons were made by sampling the incoming air for 20 min followed by sequential sampling of each of the 8 chambers for 15 min each. Average concentration of each gas during the last 5 min of each 15-min sampling period was recorded. This provided a total of 10-11 daily observations in each room. All sampling was automated. Analyzers employed for sample analyses included a TEI Model 17C ammonia/NO_x chemiluminescence analyzer and a TEI Model 45C H_2S/SO_x pulsed fluorescence analyzer (Thermo Electron Corp., Franklin, MA). Airflow (positive pressure system) through each room was measured every 30 sec using differential pressure transducers calibrated for the pressure difference across orifice plates.

Data were analyzed as a 2 x 3 factorial of 2 dietary treatments and 3 flocks (SAS v 8.0). Emissions data were adjusted for number of birds. Significance was accepted at or below a $P<0.05$.

Results and Discussion

Dietary treatment had an effect on final body weight (42 d) with broilers fed the LP treatment diets being 87 g lighter than those fed the C treatment diets (2.780 and 2.693 kg, respectively over the three flocks). Broilers fed the LP treatment diets were lighter at 42 d than those fed the C treatment diets in all three flocks but the weight differences were greatest in flock 1 (2.705 and 2.861, 2.841 and 2.907, and 2.534 and 2.573 kg for broilers fed the LP and C treatment diets in flocks 1, 2, and 3, respectively). Differences between the body weights of broilers fed the two diet treatments were evident as early as 24 d of age (1.072 and 1.101 kg for broilers fed the LP and C treatment diets, respectively). Feed consumption was lower in broilers fed the LP treatment diets resulting in no difference in FE between treatments C and LP (1.89 and 1.91, respectively over the three flocks). Mortality was similar between treatments (6%) with no flock or treatment effect observed. Others have observed decreases in body weight when diet protein is reduced (Neto et al., 2002; Bregendhahl et al., 2002) but it has been speculated (Burnham, 2005) that the decreases in performance observed by these researchers have been caused by not supplement back with sufficient amounts of limiting amino acids other than methionine and lysine. On a practical basis, however, bird performance can be hindered by excessive lowering of CP in diets due to a number of factors: reduced dietary potassium levels, altered dietary ionic balance, dediciency of nonessential amino acids, imbalances among certain amino acids (e.g. branched chain amino acids), and/or potential toxic concentrations of certain amino acids (Waldroup, 2000). These issues did not appear to be the cause for the lower body weight in the current study. Diet amino acid analysis showed that formulated and analyzed concentrations were similar. When looking at when differences started to appear and the proportrional differences at the different ages, it appears that the decrease in protein in Gr1 diet in the LP treatment may have been too severe. Despite differences in ending body weight the FCR was not affected.

In flock 3, when birds were sampled for yield determinations, treatment did not affect body weight, carcass weight, breast weight, or dress percent and breast yields. Numerical differences in body weight were similar to those seen in the three flock performance data. Body weight of sampled birds was 2.721 and 2.667 kg for broilers fed the C and LP treatment diets but because replication was low (one flock, four replicates of 20 birds per treatment) differences that were significant in the performance data were not significant in this portion of the study. Breast weights, however,were not different between broilers fed the C and LP treatment diets (542.9 and 540.7 g, respectively) and breast yields were 22.75 and 23.13% for broilers fed the C and LP treatment diets. Thus dietary treatment had no effect on breast weight or yield.

Dietary treatment affected NH_3 emissions with the LP treatment resulting in lower daily NH_3 emissions (26.5 mg kg^{-1} d^{-1} in flocks 1) compared to emissions from broilers fed the C treatments diets (33.8 mg kg^{-1} d^{-1} in flocks 1) . NO and NO_2 were also lower in the LP vs the C treatment. There was no effect of treatment on NO, NO_2, SO_2, H_2S, CO_2, CH_4, or non- CH_4 hydrocarbons. Lowering dietary protein while maintaining minimum concentrations of amino acids resulted in substantial (22%) reductions in daily emissions of NH_3 and no impact on breast weight or yield. Others have reported reduction in NH_3 when protein is reduced in the diet (Ferguson et al., 1998; Elwinger and Svensson, 1996). Elwinger and Svensson (1996) fed broilers diets containing 18%, 20% or 22% CP and measured NH_3 emissions from the litter bed. Total N losses in the houses averaged 18% to 20% of total N input. Schmidt et al., 2002 reported NH_3 emissions from turkey barns to be 592.6 and 12.3 mg kg^{-1} d^{-1}, in summer and winter, respectively. The data obtained in the current research on NH_3 emissions reflects a very dry environment since the work was during the fall and winter (September 2005 and February 2006). Litter dry matter content, that is typically between 70 and 73% in commercial houses was very high in the current study averaging 79 and 81% after flocks 1 and 2. The low moisture in litter may have contributed to a lower than expected NH_3 emissions but this can only be confirmed when litter concentrations are determined on whole nutrient balance can be calculated.

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References

Bregendhahl, K., J.L. Sell, and D.R. Zimmerman. 2002 Effect of low-protein diets on growth performance and body composition of broiler chicks. Poultry Sci. 81 1156-1167.

Burnham, D. 2005. Dietary strategies to lower nitrogen load in poultry. Proc. Can. E. Nutr. Conf. 20 pgs.

Elwinger, K. and L. Svensson, 1996. Effect of dietary protein content, litter and drinker type on ammonia emission from broiler houses. Agric. Engng. Res. 64:197-208.

Ferguson, N.S., R.S. Gates, J.L. Taraba, A.H. Cantor, A.J. Pescatore, M.L. Straw, M.J. Ford, and D.J. Burnham, 1998. The effect of dietary protein and phosphorus on ammonia concentration and litter composition in broilers. Poultry Sci. 77:1085-1093.

Mitloehner, F.M., 2005. Effects of insufficient air quality data on regulatory policy in animal agriculture. J. Appl. Poultry Res. 14:373-377.

Neto, M.G, G.M. Pesti, and R.I. Bakalli, R.I., 2002. Influence of dietary protein level on the broiler chicken's response to methionine and betaine supplements. Poultry Sci. 79: 1478-1484.

Schmidt, D.R., L.D. Jacobson, and K.A. Janni. 2002. Continuous monitoring of ammonia, hydrogen sulfide and dust emissions from swine, dairy, and poultry barns. Amer. Soc. Agric. Engineer. Meeting paper No. 024060. St. Joseph, Mich.

Waldroup, P.W., J.A. England, A.L. Waldroup, and N.B. Anthony. 1997. Response of two strains of large white male turkeys to amino acid levels when diets are changed at three-or four-week intervals. Poult. Sci. 76:1543-1555.

Total Nitrogen Deposition on Land in the Northeastern part of Romania

Cecilia Arsene[1,2], Romeo-Iulian Olariu[1], Kalliopi Violaki[2] and Nikolaos Mihalopoulos[2]

[1]Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, "Al.I.Cuza" University of Iasi, Carol I 11, 700506 Iasi, Romania

[2]Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, 714 09 Heraklion, Greece

Abstract

Recent investigations on atmospheric deposition of N-containing compounds have indicated elevated nitrogen fluxes which can significantly affect both terrestrial and aquatic ecosystems (*e.g.* soil acidification, surface-water acidification and eutrophication of aquatic systems). In most of the estimations nitrogen budgets have focused on inorganic nitrogen, despite the fact that recent works revealed significant contribution from organic N-containing species to the total N-cycle.

This is the first report on a long-time series observation (27 months) on dissolved organic nitrogen (DON) deposition on land in the northeastern part of Romania (Iasi, one of the largest urban areas in Romania). Rainwater DON was determined by the persulphate oxidation method, while inorganic-N (NO_3^- and NH_4^+) using ion chromatography. An annual mean of 45.7 μM N has been estimated as volume weighted mean for DON, while the corresponding values for NO_3^- and NH_4^+ were 42.9 and 59.7 μM N respectively. DON can thus account for a significant part (up to 30%) of the total dissolved-N. Significant correlation coefficients have been observed between organic nitrogen and species as NH_4^+ and K^+ which give a first insight on its possible sources (soil and biomass burning).

Introduction

Most of the atmospheric nitrogen species are deposited to the Earth surface via precipitation. Beside dissolved inorganic nitrogen forms (DIN) the organic forms (ON) have been shown to be also important constituents of the atmospheric N deposition (wet and dry). Wet deposition is a major source of nitrogen input to ecosystems. The increased atmospheric N deposition is mainly contributing to the alteration of the normal operating functions of the aquatic and terrestrial ecosystems in different geographical locations. Anthropogenic sources have a strong impact on the global nitrogen cycle with most of the human activities responsible for the increase in global nitrogen being local in scale (*i.e.*, production and use of nitrogen fertilizers, burning of fossil fuels, power generation plants and industries).

Deposition of inorganic N-containing compounds has been found to be much higher in Romania than in any many other regions in Europe (Arsene et al., submitted to Atmospheric Environment, 2006). However, very little is known about the characteristics of nitrogen sources, rates of input and removal, and the effects of nitrogen deposition on the environment. This work reports on a long-time series observation (27 months) of total dissolved nitrogen (TDN) deposition on land in the north eastern part of Romania (Iasi, one of the largest urban areas in Romania).

Methods

Details in the analysis of inorganic species by ionic chromatographic method can be found in Economou and Mihalopoulos, 2002. The determination of DON in rainwater was made on the base of the total nitrogen measurements from which the DIN fraction concentration was subtracted. Persulfate oxidation-based conversion (wet chemical) of organic N to nitrate which is among other reliable measurement techniques (*i.e.*, UV photolysis and high-temperature catalytic oxidation techniques) was used for DON quantification.

This method was found to be more efficient at converting organic-N compounds to NO_3^- although the final results can be affected by significant non-systematic losses depending upon sampling, storage and analysis procedures (Scudlark et al., 1998). However, with appropriate optimization this method can give reliable results (Bronk et al., 2000). Comparison studies of the data obtained by different independent measurement techniques, *i.e.* UV and persulphate oxidation methods, indicates that the observation of the rainwater DON concentration is not the result of an analytical artifact (Cornell and Jickells, 1999).

Results and Discussion

Figure 1 shows the geographical location where the sampling procedure has been undertaken from May 1, 2003 to July 31, 2005 (47°20″ northern latitude and 27°60″ eastern longitude geographical coordinates).

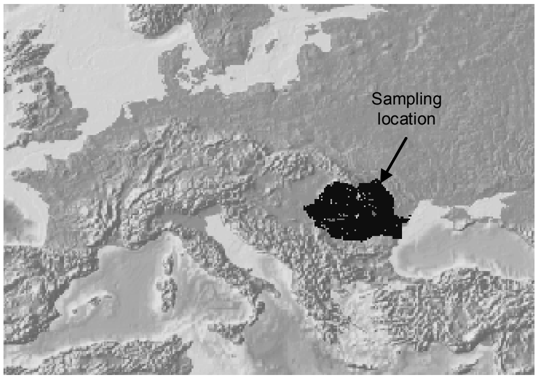


Figure 1. Location of the sampling site

Individual trajectory plots of the air masses origin were examined in details for all the period of interest. Five day backward trajectories were calculated in order to identify the most likely travel path of air masses affecting the surveyed region. The prevalence of air masses originating from the northern sector (N-NE-NW) with contribution from 40 – 60% over a year is the most obvious feature. Most of the raining events occurred in air masses originating from that sector.

The samples collected from May 2003 to July 2005 have been subjected to analysis for various nitrogen species and pH. Figure 2 shows the distribution both of pH and temperature over the study period. The mean pH value over a year is close to 5.6.

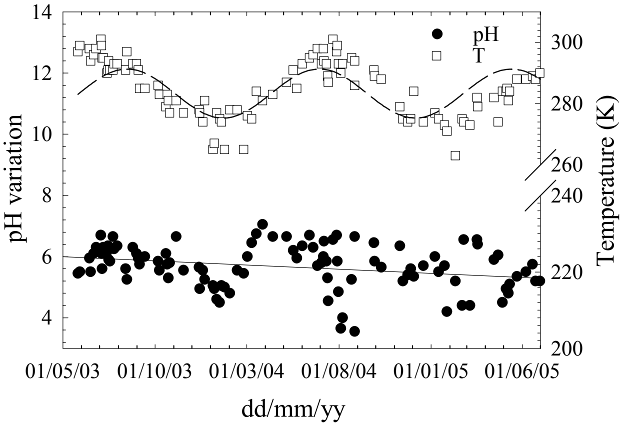


Figure 2. Variation of the temperature at the sampling site and rainwater pH distribution

Based on the volume weight mean (VWM) concentration inorganic nitrogen identified as NO_3^- and NH_4^+ appears to be the dominant fraction of N representing 70% of the total nitrogen. Ammonium concentration in the analysed rainwater samples ranged from 22.4 μM N to 155.1 μM N (mean value 59.7 μM N) while

NO_3^- ranged from 6.2 µM N to 93.8 µM N (mean value 42.9 µM N). For organic nitrogen the VWM concentration is found to be 45.7 µM N with a range from 14.2 µM N to 174.8 µM N.

Each of the quantified nitrogen-containing compound correlate well with the rain amount indicating these species are washed out of the atmosphere by rainfall. From the interspecies correlation analysis is obvious the correlation between DON and NH_4^+ which would suggest that these N species might have similar source in rainwater (Figure 3). Significant correlations have been observed between DON and K^+ as Figure 3 shows.

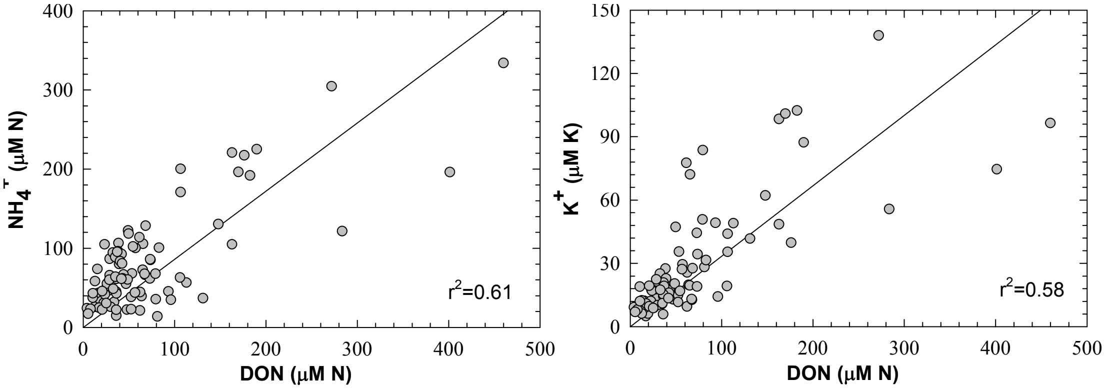


Figure 3. Correlation between concentration of DON and species like NH_4^+ and K^+

The VWM concentrations of N-containing species identified in rainwater collected at Iasi from May 2003 to July 2005 (seasonal variation) are given in Table 1. Seasons are defined as follows: winter December 1 – February 28, spring March 1 – May 31, Summer June 1 – August 31, autumn September 1 – November 30.

Table 1. VWM concentration of N-containing species in rainwater collected at Iasi, Romania.

	µM N DON	µM N NH_4^+	µM N NO_3^-	µM N TDN	DON (%) relative to TDN
Average	45.7	59.7	42.9	148.3	30.8
Winter	40.4	79.7	47.7	168.8	27.2
Spring	39.4	34.9	46.7	121.0	26.6
Summer	48.6	61.2	46.2	156.0	32.8
Autumn	54.4	62.8	31.3	148.5	36.7

The winter maximum concentration for NH_4^+ is most probable due to the application of fertilisers. In Romania during winter alternative cold and warm seasons occur so that sometimes the agricultural activities (especially application of fertilisers) peak during this season. The VWM concentration of DON was at maximum during summer and autumn but at the moment is difficult to make an assumption of the possible sources likely responsible for these peaks.

Figure 4 depicts fluxes variation of the identified N-containing species in order to better identify potential seasonal differences in N speciation.

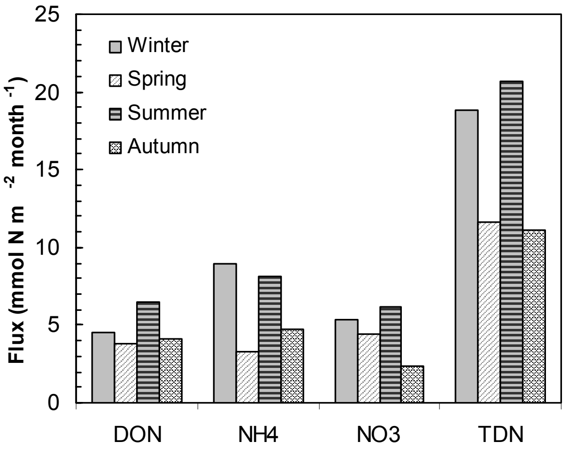


Figure 4. Fluxes of the various analysed N-containing species during different seasons

Conclusions

Rainwater collected between May 2003 and July 2005 was analyzed in order to identify inorganic and organic fraction of the nitrogen containing compounds. Inorganic nitrogen is the dominant form of N representing as high as 68 – 70 % of total nitrogen based on the monthly VWM concentrations. The results presented here suggest that DON also contributes a large fraction of total water soluble N in precipitation across Iasi region. It has been showed that DON concentrations are strongly correlated across the monitored site with those of NH_4^+, implying possible common sources. Elevated nitrogen-containing compounds concentrations like those observed in the monitored area might have a strong impact on terrestrial and aquatic ecosystems in the area so that an accurate quantification of the deposition fluxes of atmospheric N will be of a great importance for reliable predictions of the impacts.

References

Arsene, C., R.I. Olariu, Z. Markaki, P. Zarmpas, G. Kouvarakis, and N. Mihalopoulos. 2006. Chemical composition of rainwater in the northeastern Romania (Iasi). Submitted to *Atmospheric Environment*.

Bronk, D.A., M.W. Lomas, P.M. Glibert, K.J. Schukert, and M.P. Sanderson. 2000. Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high-temperature oxidation methods. *Marine Chemistry* 69: 163-178.

Cornell, S.E., and T.D. Jickells. 1999. Water-soluble organic nitrogen in atmospheric aerosol: a comparison of UV and persulfate oxidation methods. *Atmospheric Environment* 33: 833-840.

Economou, C., and N. Mihalopoulos. 2002. Formaldehyde in the rainwater in the eastern Mediterranean: occurrence, deposition and contribution to organic carbon budget. Atmospheric *Environment* 36: 1337-1347.

Scudlark J.R., K.M. Russell, J.N. Galloway, T.M. Church, and W.C. Keene. 1998. Organic nitrogen in precipitation at the mid-Atlantic U.S. Coast-methods evaluation and preliminary measurements - a new high-temperature combustion method and a comparison with photo-oxidation. *Atmospheric Environment* 32: 1719-1728.

How Do Property-Line Concentrations of Feedyard PM_{10} Vary with Time of Day, Season and Short-Term Weather Phenomena?

Brent Auvermann[1,2], K. Jack Bush[2], and Billy Chaffin[2].
[1]Texas Cooperative Extension, Texas A&M University, Amarillo, TX 79106, USA
[2]Texas Agricultural Experiment Station, Texas A&M University, College Station, TX 77843, USA.

Abstract

We present particulate-matter concentration data from a long-term, quasi-continuous monitoring project around the perimeter of a commercial cattle feedyard in the Southern High Plains. Ground-level PM_{10} concentrations vary seasonally and diurnally as well as in response to short-term weather patterns. The data provide a suitable basis for annualizing PM_{10} emission factors originally derived from short-term, worst-case monitoring campaigns.

An Early Look at "Integrated Corral Management" as a BMP for Feedyard Dust Control

Brent Auvermann[1,2], Thomas Marek[2], and Graham Hartmann[1]
[1]Texas Cooperative Extension, Texas A&M University, Amarillo, TX 79106, USA
[2]Texas Agricultural Experiment Station, Texas A&M University, College Station, TX 77843, USA.

Abstract

The economic value of fugitive dust control from cattle feedyards is an elusive quantity, which makes it difficult to assign cost/benefit analysis to Best Management Practices (BMPs). Integrated Corral Management is a means of leveraging existing feedyard-management approaches by putting advanced communications and software technologies into the hands of employees who are in the best position to provide feedback on environmental quality. These technologies give the feedyard manager new and more efficient options to integrate environmental considerations, including air quality, into the day-to-day, profit-oriented operation of a cattle feedyard.

Visibility Measures Can Be Used To Estimate Feedyard Dust Concentrations

Brent Auvermann

Texas Cooperative Extension and Texas Agricultural Experiment Station, Texas A&M University, Amarillo, TX 79106, USA

Abstract

Path-averaged measurements of total atmospheric extinction are a reasonable surrogate for mass concentration measurements of particulate matter (PM_{10} and TSP) downwind of cattle feedyards, provided that one accounts for the effect of relative humidity on the particles' refractive properties.

A Comprehensive Analysis of the Evening Dust Peak at Cattle Feedyards

Brent Auvermann[1], Bryan W. Shaw[2], and Todd E. Stiggins[2]
[1]Texas Cooperative Extension and Texas Agricultural Experiment Station, Texas A&M University,
Amarillo, TX 79106, USA
[2]Department of Biological and Agricultural Engineering, Texas A&M University,
College Station, TX 77843, USA.

Abstract

The well documented peak in ground-level, fugitive dust concentrations that occurs near cattle feedyards in the mid- to late evening is a consequence of three primary factors: an increase in animal activity, an increase in atmospheric stability and a diurnal minimum in the moisture content of the uncompacted manure on the corral surface. We present a theoretical model to explain this phenomenon and to provide a rational basis for estimating the importance of each of those factors in predicting the ground-level, property-line concentration of PM_{10} at a given time of day. We also present preliminary data to illustrate animal behavior patterns in the cattle feedyard.

Ammonia Emissions and Dry Deposition Studies at Some Hog Farms in North Carolina

Kanwardeep S Bajwa, S. Pal Arya and Viney P Aneja
Dept of Marine, Earth and Atmospheric Sciences,
North Carolina State University,
Raleigh, NC 27695-8208, USA

Abstract

Experimental and modeling studies have been conducted on emissions, dispersion and dry deposition of ammonia taking one swine farm as a unit. Ammonia emission fluxes were measured during the years of 2002 to 2004. Measurements of ammonia flux were made at 11 swine facilities in North Carolina using a dynamic flow-through chamber system over the anaerobic waste treatment lagoons and other water holding structures, and each farm was measured during two 8-10 day periods representing warm and cold seasons. Barn emissions were also measured during those periods. Flux data was used to validate a process based Coupled mass transfer and chemical reaction model and an Equilibrium model developed by Aneja et al., (2001a) to better understand emission processes from lagoon surface. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. Emission data from lagoon and barns is used to study short range downwind dispersion and dry deposition of ammonia from selected swine facilities using USEPA's AERMOD model.

Introduction

Ammonia is an important atmospheric pollutant that plays a key role in several air pollution problems. Ammonium salts remain a major component of inorganic atmospheric aerosols and thus NH_x (NH_x = ammonia + ammonium) plays a major role in the physical and chemical processes of the atmospheric nitrogen cycle (Warneck, 1999). Ammonia is gaining increasing importance, as a principle source of atmospheric aerosols (Baek et al, 2004). Gaseous ammonia undergoes dry deposition with deposition velocities ranging up to 14 cm/s (Phillips et al., 2004). Due to its high deposition velocity and its reactivity in the atmosphere, gaseous ammonia has a relatively short atmosphere lifetime, on the order of a few days or less (Warneck, 1999). NH_3 emissions from source region, primarily evolving from swine and poultry operations, are found to increase NH_4^+ concentration in precipitation at site up to ~ 80 km away (Walker et al., 2000). Results presented in NCDENR report (1999) demonstrate that ammonia (NH_3) emissions from swine production facilities can significantly enhance dry deposition of NH_4-N to adjacent forest canopies. Phillips (2003) showed that NH_3 contributed 47% of the total nitrogen dry deposited in the Neuse river watershed.

With the increasing human demand for food production, the use of nitrogen containing fertilizers and production of domestic livestock is increasing. Domestic animal waste is the major source of ammonia emissions. (Warneck,1999). Air mass trajectories suggest that wet and dry deposition of ammonia and ammonium emitted from agricultural operations in eastern North Carolina could potentially affect all river basins in the coastal plain region, as well as sensitive coastal ecosystem and estuaries (Walker et al., 2000). Such ecosystems are subject to potential environmental consequences, including aquatic eutrophication and soil acidification. High N-loading can also have detrimental effects in terrestrial ecosystems, effects that can result in the greater export of N to surface and groundwater.

Quantification of NH_3 emissions and deposition is necessary in order to assess the potential extent of such environmental effects. For reduction strategies to put in place, we need to know the total budget of ammonia and contribution of various sources. Livestock waste emission estimates used by EPA are based on emission factors recommended in a 1994 study by Battye et al.(1994) ,which are derived from European measurements, where animal practices may vary significantly from United states. Battye et al (2003) shows that livestock waste contribute from 80-89% of ammonia emissions in North Carolina. Emission rates from lagoons are difficult to measure, requiring specialized equipment. An emission model to predict ammonia emissions would reduce the expense of determining emissions on the large number of lagoons.

Measurements of ammonia flux from hog waste treatment lagoons (Aneja et al., 2001b; Aneja et al., 2000) and from fertilized and unfertilized soils (Roelle , 2001) have been made and analyzed with respect to corresponding environmental parameters, including lagoon and soil temperature, pH and TAN (Total Ammoniacal Nitrogen). Harper et al (2004) studied the ammonia emissions from hog lagoons using micrometeorological technique. Todd et al (2001) used a network of open-path fourier transform infrared (FTIR) optical ray method to measure ammonia emission rates from the hog lagoon. Studies have also been done to model ammonia emissions. Asman et al (1998) reviewed the ammonia research, process description and emission factors for ammonia emissions. Koelliker and Minor (1973) developed desorption model for ammonia emissions using two film theory. The overall mass transfer co-efficient (Halsam et al, 1924) in this model depends on wind velocity and temperature. This gives an emission of zero under calm conditions with no wind. Olsen and Sommer (1993) modeled ammonia emissions from stored slurry considering effects of wind speed and surface cover. A model to predict ammonia volatilization from flooded soils using total ammoniacal nitrogen (TAN), pH, temperature, floodwater depth and wind speed was developed by Jayaweera and Mikkelsen (1990). De Visscher et al (2002) developed a two layer model to study emissions from anaerobic lagoon. The model uses effluent concentration, water temperature, wind speed and effluent pH. Aneja et al (2001a) developed a Coupled mass transfer and chemical reactions model and Equilibrium model to simulate ammonia emissions from swine waste lagoons. This two layer model takes into account two film theory using molecular transfer of ammonia across the lagoon-air interface. It also takes into account pseudo-first order reaction of ammonia with water and acidic species (H_2SO_4, HNO_3, HCl) in the atmosphere. It incorporates air temperature, lagoon temperature, pH, wind speed, TAN and ambient ammonia concentration. This model shows exponential increase with lagoon temperature and pH and linear increase with wind speed and TAN.

This study includes comparisons of measured ammonia emission fluxes from swine waste treatment lagoon systems and modeled ammonia emission fluxes using both the Coupled and Equilibrium models developed by Aneja et al (2001a). Comparison of measured and modeled emission fluxes will help us to validate the model and also help us to make improvements in model or measuring techniques of required parameters in this model. This study will also focus on dispersion and dry deposition of ammonia downwind of swine facilities, to quantify ammonia dry deposition downwind of selected hog farms.

Sampling and Measurement

As a part of project OPEN (Odor, Pathogens and Emissions of Nitrogen), ammonia flux measurements were made at 11 swine farm operations in eastern North Carolina. The waste from the hog sheds was flushed out with recycled lagoon water and discharged back into the waste lagoon from the top, often with additional treatment using potential Environmentally Superior Technologies (ESTs). Each farm was sampled twice between 2002 and 2004, one representing the warm season and the other representing the cold season. Only the lagoon component of hog farm was investigated in this study. Fifteen minutes averaged measurements were made for ammonia flux and environmental data. This data was then averaged to one hour period for use in this study.

A flow through dynamic chamber system with a variable-speed continuous impeller was used to measure NH_3 emissions from lagoon surfaces (Aneja et al., 2000; Chauhan 1999; Kim et al., 1994). A Thermo Environmental Instrument Incorporated (TECO) Model 17C chemiluminescnce ammonia analyzer was used to monitor ammonia concentration during ammonia flux measurement periods. A 10 m meteorological tower was erected at each site to measure wind speed and direction, temperature and relative humidity. Wind speed and direction were measured at 10 m above the surface. Air temperature and relative humidity (RH) measurements were made at 2 m height. The pH and temperature probes were placed in the lagoon at depths of 15-20 cm. Lagoon water samples were collected daily from measurement sites and were analyzed for total ammoniacal nitrogen (TAN).

Mass Transport models

Two process-based models were developed by Aneja et al (2001a) to determine ammonia flux from a lagoon-air interface. The principle characteristic of these models are the two thin layers or films of air and liquid above and below the air-liquid interface for molecular exchanges between water and air, respectively (Whitman and Davis, 1923, Cussler 1996). All the resistance to mass transfer across the interface is due to the thin layer in which molecular transfer takes place. The steady state molecular diffusion equation for a horizontally homogenous thin layer in the liquid or gas (air) adjacent to the air-liquid interface is given by Arya (1999);

$$D_i \frac{d^2 C_i}{dz^2} = k_{ri} C_i \qquad (1)$$

where C_i is the concentration of the diffusing material, z is the vertical distance from the interface, D_i is the molecular diffusivity, and k_{ri} is the reaction constant for ammonia in the liquid or gas phases such that $D_i = D_L$ and $k_{ri} = k_{rL}$ for liquid and $D_i = D_a$ and $k_{ri} = k_{ra}$ for air, respectively.

If we neglect chemical reactions in the two films, a simple equilibrium model can be derived from equation 2. Coupled Mass Transfer with Chemical Reactions Model (Coupled model) takes into account molecular diffusion and some chemical reactions. In the liquid film, only ammonia's reversible reaction in the water is considered, and pH is assumed constant. For the air film, the primary reactions of ammonia with sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), water, and the hydroxyl radical (OH) are considered (Finlayson-Pitts and Pitts, 2000; Warneck, 1999). Further details of these models are given by Bajwa et al (2006).

Results and Discussions

The Coupled mass transfer and chemical reaction model and the Equilibrium model show strong dependence on lagoon temperature, lagoon pH, total ammoniacal nitrogen (TAN) and wind speed. The modeled ammonia flux increases exponentially with the increase in lagoon temperature. Lagoon temperature affects the Henry's law coefficient, the liquid phase diffusivity of ammonia and ammonium, the dissociation constant, and viscosity and density of the liquid layer. The pH of a waste treatment lagoon controls the chemical equilibrium between ammonia and ammonium, and an increase in pH increases the fraction of ammonia in the solution. With an increase in pH, both models show an exponential increase in ammonia flux. Lagoon TAN controls the concentration of ammonia in lagoon water. Any increase in lagoon TAN gives a corresponding linear increase in ammonia flux. Since the air film is a laminar sub-layer, it is affected by meteorological and environmental parameters such as wind speed and stability. Thus wind speed may also affect ammonia emissions. Sensitivity analysis of both models shows a polynomial (nonlinear) relationship between ammonia flux and wind speed. Air temperature and ambient ammonia concentration did not show any significant effect on the ammonia flux for both the models (Bajwa et al).

Ammonia flux and most of the lagoon and environmental data were averaged over 15 minute intervals during the measurements periods for both the warm and cold seasons. But for the present analysis, those data were further averaged for 1 hour periods. Although flux measurements were made for longer periods, only those hourly data are used for which all the required meteorological parameters (wind speed and air temperature) and lagoon parameters (lagoon pH, lagoon temperature and total ammoniacal nitrogen) were available.

Various statistical measures have been proposed and utilized for evaluating the performance of air quality and dispersion models (see e.g., Irwin, 1983). Here, we have used a few simple statistical parameters, such as mean bias (MB), normalized mean bias (NMB), and normalized root-mean-square error (NRMSE) as given by Irwin (1983). These statistics were calculated for both the warm and cold seasons, separately, as well as for the combined data set.

Table 1 compares the mean flux, mean bias, normalized mean bias and normalized root-mean-square-error (NRMSE) for both the Equilibrium and Coupled models. These model performance statistics indicate slight superiority of the simpler Equilibrium model over the more complicated Coupled mass transfer with chemical reactions model. Percentages of hourly model predicted fluxes that are within a factor of two of the observed hourly fluxes are comparable for the two models; these are less than 45%. We have also examined separately the cases of gross over and under predictions (by more than a factor of 5) by the Equilibrium model.

Table 1 Statistical performance parameters for Equilibrium and Coupled models

Statistical Parameter	Equilibrium Model prediction			Coupled Model Prediction			Observed		
	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data
Number of Hours (N)	706	868	1574	706	868	1574	706	868	1574
Mean Flux (μg NH_3-N/m^2-min)	1150.8	944.8	1037.2	2210.8	1391.3	1758.9	1545.1	538.1	989.7
Mean Bias (μg NH_3-N/m^2-min)	-394.3	406.8	47.5	665.7	853.3	769.1	-	-	-
Normalized Mean Bias	-0.26	0.76	0.05	0.43	1.59	0.78	-	-	-
NRMSE	1.76	1.96	2.01	3.58	2.69	3.90	-	-	-
% Within a Factor of 2	38	43	41	45	41	43	-	-	-

Conclusions and Future Work

Ammonia flux measurements were made on swine waste treatment lagoons using a dynamic flow through chamber system. Hourly averages of wind speed, lagoon temperature, TAN, lagoon pH and air temperature were used as inputs into the two thin-film mass transfer models to predict ammonia flux and these predictions were compared with hourly averaged values of measured ammonia flux. Measurements made in the warm and cold season were analyzed and modeled separately to look into the seasonal differences between measured and predicted ammonia fluxes. Measured ammonia fluxes were higher in the warm season as compared to the cold season as high lagoon temperatures in the warm season lead to increased ammonia fluxes.

Both the Equilibrium model and the Coupled mass transfer with chemical reactions model predicted ammonia flux reasonably well in both seasons. Observed ammonia flux falls between predicted fluxes by the Equilibrium and Coupled models in the warm season, while both models overpredicted ammonia flux in the cold season. Equilibrium model predictions gave lower value of NRMSE and bias than the Coupled model predictions in both seasons. Average of predicted fluxes by both models were within a factor of two of observed fluxes in both the warm and cold season, except by the Coupled model in the cold season when the mean was more than twice the observed flux. Equilibrium model gave more consistent results as NRMSE and bias varied less between both seasons as compared to the Coupled model results.

Further analysis of data available from all 11 farms will be carried out to validate Coupled mass transfer and chemical reaction model and Equilibrium model. More statistical analysis of modeled and measured flux will be done to calculate over prediction or under prediction by models to measure accuracy of predicted values. We will also examine separately the cases of gross over and under predictions (by more than a factor of 5) by the Equilibrium model. AERMOD model will be used to study dispersion and dry deposition of ammonia downwind of some swine facilities.

References

Aneja, V.P., J. P. Chauhan, and J. Walker,. 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *Journal of Geogphysical Research (Atmospheres)* 105: 11535-11545.

Aneja, V. P., B.P. Malik, Q. Tong, D. Kang, and J.H. Overton. 2001a. Measurement and modeling of ammonia emissions at waste treatment lagoon-Atmospheric Interface. *Water, Air and Soil pollution: Focus* 1: 177-188

Aneja, V.P., P.A Roelle, G.C. Murry, J. Souterland, J.W. Erisman, D. Fowler, W.A.H Asman, and N. Patni. 2001b. Atmospheric nitrogen compounds II: emissions, transport , transformation, deposition and assessment. *Atmospheric Environment* 35: 1903-1911.

Arya, S.P. 1999. Air pollution meteorology and dispersion. Oxford University Press, New York.

Asman, W.A.H., P. Ceiller, S. Genermont, N.J. Hutching, and S.G. Sommer. 1998. Ammonia emission research: From emission factors to process description. *Eurotrac Newsletter* 20: 2-10.

Baek, B.H., V.P. Aneja, and Q. Tong. 2004. Chemical coupling between ammonia, acid gases, and fine particles. *Environmental Pollution* 129: 89-98.

Bajwa, K.S., V.P. Aneja and S.P. Arya (2006). Measurement and estimation of ammonia emissions from lagoon-atmosphere interface using a coupled mass transfer and chemical reactions model, and an equilibrium model. *Atmospheric Environment* (In press).

Battye, R., W. Battye, C. Overcash, and S. Fudge. 1994. Development and selection of ammonia factors. EPA/600/R-94/190, Final Report Prepared for US Environmental Protection Agency, Office of Research and Development, EPA Contract No. 68-D3-0034, Work Assignment 0–3.

Battye, W., V.P. Aneja, and P.A. Roelle. 2003. Evaluation and improvement of ammonia emissions inventories. *Atmospheric Environment,* 37: 3873-3883.

Chauhan, J.P. 1999. Characterization of the ammonia emissions from swine waste storage and treatment lagoons. MS thesis, North Carolina state University, Raleigh, NC, USA.

Cussler, E.L. 1996. Diffusion: Mass transfer in fluid systems. Cambridge University Press, New York. pp 580.

De Visscher A, L.A. Harper, P.W. Westerman, Z. Liang, J. Arogo, R.R. Sharpe, and O. Van Cleemput. 2002. Ammonia emissions from anaerobic swine lagoons: Model development. *Journal of Applied Meteorology*. 41, 426-433.

Finlayson-Pitts, B.J. and J.N. Pitts Jr. 2000. Chemistry of Upper and Lower Atmosphere: Theory, Experiments and Applications. Academic Press, San Diego, CA.

Halsam, R.T., R.L. Hershey, and R.H. Keen. 1924. Effect of gas velocity and temperature on rate of absorption. *Industrial and Engineering Chemistry Research* 16: 1224-1230.

Harper, L.A., R.R. Sharpe, T.B. Parkin, A. De Visscher, O.V. Cleemput, and F.M. Byers. 2004. Nitrogen Cycling through Swine Production Systems: Ammonia, Dinitrogen, and Nitrous Oxide Emissions. *Journal of Environmental Quality* 33: 1189-1201.

Irwin, J. S. 1983. Estimating plume dispersion – A comparison of several sigma schemes. *Journal of Climate and Applied Meteorology* 22: 92-114.

Jayaweera, G.R., and D.S. Mikkelsen. 1990. Ammonia volatilization from flooded soil systems: A computer Model, I. Theoretical aspects. *Soil Science Society of America Journal* 54: 1447-1455.

Kim, D.S., V.P. Aneja, and W.P. Robarge. 1994. Characterization of nitrogen oxide fluxes from soils of fallow fields in the coastal piedmont of North Carolina. *Atmospheric Environment* 28: 1129-1137.

Koelliker, J.K., and J.R Minor. 1973. Desorption of ammonia from anaerobic lagoons. *Transanction of ASAE* 16: 148-151.

North Carolina Department of Environment and Natural Resources (NCDENR). 1999.

Status report on emissions and deposition of atmospheric nitrogen compounds from animal production in North Carolina. June 7, 1999, Raleigh, NC.

Olsen, J.E., and S.G. Sommer. 1993. Modeling effects of wind speed and surface cover on ammonia volatilization from stored pig slurry. *Atmospheric Environment* 27A(16): 2567-2574.

Philips, S.B. 2003. Measurements, modeling and analysis of fluxes of nitrogen compounds. PhD Thesis, North Carolina State University, Raleigh, NC.

Philips, S.B., S.P. Arya, and V.P. Aneja. 2004. Ammonia flux and dry deposition velocity from near-surface concentration gradient measurements over a grass surface in North Carolina. *Atmospheric Environment* 38: 3469-3480.

Roelle, P.A. 2001. Oxidized and reduced biogenic nitrogen compound emissions into the rural troposphere: Characterization and Modelling. PhD thesis, p 11. North Carolina State University, Raleigh, NC.

Todd, L. A., M. Ramanathan, K. Mottus, R. Katz, A. Dodsen, and G. Mihlan. 2001. Measuring chemical emissions using open path Fourier transform infrared (OP-FTIR) spectroscopy and computer-assisted tomography. *Atmospheric Environment* 35: 1937-1947.

Walker, J.T, V.P. Aneja, D.A.and Dickey. 2000. Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment* 34: 3407-3418.

Whitman, W.G., and D.S. Davis. 1923. Comparative absorption rates of various gases. *Chemical and Metallurgical Engineering* 29: 146.

Warneck, P. 1999. Chemistry of the Natural Atmosphere. International Geophysical Series 71, Academic Press Inc., San Diego.

Odor Emission Reduction from Enclosed Growing-Finishing Pig House Using Different Biofilter Media

J.I. Song[1], Y.H. Yoo[1], T.I. Kim[1], Antonio J. Barroga[2], H.C. Choi[1], J.W. Jeong[1], K.Y. Yeon[1], C.B. Yang[1], D.H. Kim[3], and J.W. Lee[4]

[1]RDA – National Livestock Research Institute, Suwon, 441-350, Korea;
[2]Department of Animal Science, Central Luzon State University, Science City of Munoz, Nueva Ecija, Philippines
[3]Department of Animal Resources Technology, Chinju National.University;
[4]Gyeongnam Province Advanced Swine Research Institute.

Abstract

This study was conducted to determine the odor reduction efficiency of a biofilter design using different filter materials. The summary of results are as follows; 1.The airflow penetration rate of the different filter materials namely; rice straw, woodchips, rice hulls and sawdust were 0.72 m/s, 0.64 m/s, 0.48 m/s and 0.17 m/s, respectively. 2. Compared to a pig barn with no biofilter, NH_3 emission was reduced by 77 % using a biofilter media of sawdust and wood chip followed by rice hull and rice straw with a removal efficiency of 69% and 46%, respectively. Based on a two bi-weekly monitoring of NH_3 emission, wood chips as a biofilter media proved to be the most superior and consistent in reducing this gas due to removal efficiencies of 76 %, 55% and 76% for days 7, 14 and 36’ respectively. On the other hand, rice hull was the most effective among biofilter media in reducing H_2S with 86.27 % removal efficiency during a two consecutive bi-weekly monitoring period. The above findings also demonstrated that H_2S could be easily trapped/absorbed effectively by all the biofilter media than NH_3. Finally, the airflow penetration rate of the different biofilter media tended to be related to odor elimination efficiency with having the slowest penetration rate of 0.17 m/s.

Introduction

A biofilter is a bed of organic material (rice straw, sawdust, rice hull, wood chips etc) where odorous air can passed through (Fig, 1). It is important however that the right moisture in the filter material should be attained for the survival of microbes that are naturally present in the different filter media. The material filters dust from the air and serves as a host for microbes that convert odorous gases into non-odorous gases. Analysis of livestock odor (there are around 411 odor causing compounds) has been done during the last 30 years and majority of them were identified and described by Wright et al (2005). Song et al. (2005) was able to quantify a reduction in daily gain and feed conversion efficiency of pigs (5 kg to 31 kg) by 22 % and 9 %, respectively when indoor $NH_{3\ \text{was}}$ increased from 3.73 mg/liter to 4.91 mg/l.

The effectiveness of the biofilter depends upon the length of stay of the odorous air in the filter long enough for the odorous gases to be trapped on the medium containing the microbes to neutralize the malodor compounds by way of biochemical reaction. Two gases typically found in air from swine facilities are hydrogen sulfide and ammonia, and properly operating biofilters can remove 80 to 95% of those gases.

It is on this premise that, varying biofilter media were assessed to determine their varying removal efficiencies of malodors from an enclosed pig barn.

Methods

The biofilter was installed in a two-storey high-rise enclosed pig barn (HRHB) at the National Livestock Research Institute in Suwon, South Korea. The HRHB has an air flow capacity of 7,200 m^3/h and and the size of the exhaust fan is 630 mm. On the other hand, the biofilter had a width of 2,000 mm, length of 2,400 ppm and height of 600 mm. The duct size was 730 mm. The NH_3 gas was collected using a handy gas sampler (Gastec GV-100, Shimoto, HS-7) (Figs 1 and 2) capable of detecting 0~30 mg/ℓ and 0~1,000 mg/ℓ for NH_3 and CO_2, respectively and measured by Gas Chromatography. The bedding materials used were rice hull, rice straw, saw dust and wood chip. The periodic changes when the indoor air, which served as the control, was sucked out and allowed to pass through the different biofilter media was monitored on days 7, 21 and 36.

Results and Discussion

In terms of persistency of the different filter media in neutralizing the malodors, woodchip proved to be the most effective in neutralizing NH_3 gas as it had the lowest concentration on the 36th day at 10.7 □/□, followed by sawdust, rice straw and rice hull at 12.3 □/□, 21.5 □/□and 35.3 □/□, respectively. Therefore, woodchips were able to reduce almost 80% of the NH_3 gas inside the pig house, which means a significant improvement in the quality of air to be borne by the neighborhood.

Table 1. Periodic NH_3 concentration changes after biofilter media penetration*

Items	Duration, days		
	7	21	36
Indoor pig house[1)]	7.6	12.3	51.9
Rice hull, □/□	2.7	19.2	35.3
Rice straw, □/ℓ	4.3	7.5	21.5
Sawdust, □/ℓ	1.8	5.5	12.3
Wood chip,□/ℓ	2.2	17.6	10.7

*Measured by gas chromatography

1) Exhaust gas concentration

Likewise, in terms of persistency rate for the entrapment of the H_2S by individual biofilter media rice hull was the most consistent during the two consecutive bi-weekly monitoring at 86.27% followed by wood chip, saw dust and rice straw with values of 84.66%, 79.53% and 62.08%, respectively. The high carbon nature of the rice hull and wood chip as compared to the other media apparently contributed to effective absorption and utilization of the microbes in the biofilter media.

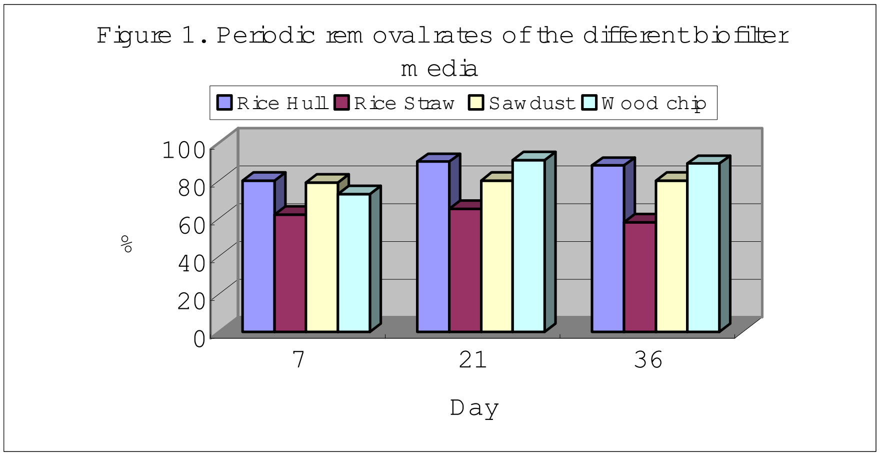


Figure 1. Periodic removal rates of the different biofilter media

In terms of on the spot dust and gas entrapment, (Table 3) by the individual filter media, the absorption of NH_3 was very effective in both the sawdust and wood chip biofilter media as their recovery of the gas amounted to 3 □/□in contrast to rice hull and rice straw which is 4 □/□and 7 □/□, respectively. It is interesting to note also that H_2S, which is one of the most offensive odors, was no longer detected in the rice hull, sawdust and woodchip filter media, while in the rice straw it was barely detected. Being the least dense among the filter media, it was expected that dust level was the highest in the rice straw. Woodchip on the other hand prove to be the most effective in absorbing CO_2 although this is not given emphasis in the study, as it is not considered a malodor. However, prolonged exposure of this gas inside livestock houses can be detrimental also to the health of animal caretakers.

Table 3. Concentration of gas and dust after penetrating the different biofilter media

Items	NH_3, □/ℓ	H_2S, □/ℓ	Dust, □/ /m^3	CO_2, □/ℓ
Indoor pig house*	13	4	93	780
Rice hull	4(69.23) ***	N.D**.	53(43.01)	510(34.61)
Rice straw	7(46.15)	1(25)	99(6.45)	550(29.48)
Sawdust	3(76.92)	N.D.	38(59.21)	380(51.28)
Woodchip	3(76.92)	N.D.	41(44.08)	470(39.74)

*Reference value
**Not detected
***All values in parenthesis are reduction values relative to indoor pig house level

Conclusions

It is therefore clear that based on our confirmatory experiments, biofilter is very effective in reducing malodors and with the abundance of rice straw, rice hull, sawdust and wood chips, there is no reason why we cannot adapt this as part of a livestock waste management strategy. Various agencies in our government can promote biofilter to both the backyard and commercial sectors. Meanwhile, companies in the contract growing franchise for broilers and hogs can recommend biofilter as part of their housing innovations as the added investment which is very minimal can be offset by the improvement in the growth when malodors particularly ammonia is reduced

References

Song J.I. ,H. L. Choi, H.C. Choi, T.I. Kim , A.J. Barroga and C.B. Yang. 2005. Environmental effects of natural and forced ventilated nursery pig houses.Unpublished.

Wright, D.W., Eaton, D.K., L.T. Nielsen, F.W. Kuhrt, J.A. Koziel, J.P. Spinhirne and D.B. Parker. 2005. Multidimensional gas chromatography-olfactometry for identification and prioritization of malodors from confined animal feeding operations. Journal of Agriculture and Food Chemistry. Accepted for Publication.

A Field Survey on Concentration of Odor Compounds in Pig Buildings and Boundary Areas

Y.H. Yoo[1], T.I. Kim[1], J.I. Song, Antonio J. Barroga[2], J.W. Jeong[1], H.C. Choi[1], C.B. Yang[1], Y.K. Jang[3], H.J. Kim[3], and K.P. Song[3]

[1]RDA – National Livestock Research Institute, Suwon, 441-350, Korea
[2]Central Luzon State University, Science City of Munoz, Nueva Ecija, Philippines
[3]University of Suwon, Korea

Abstract

A field survey was done to determine the levels of odor emission from pig buildings and quantify the odorants and their respective reduction rates when detected 20 meters within the boundary area. The odorants were measured from large, medium and small farms with enclosed and open housing systems and slurry and sawdust manure fermentation treatment methods. Among the odorous matters investigated, NH_3 had the highest emission level at 0.9 to 21 ppm; followed by Hydrogen Sulfide(H_2S) with a highly varied concentration of 51.9 to 6,712.4 ppb , methylmercaptan (CH_3SH) ranging from non-detectable level (ND) to 27.64, dimethylsulphide ($(CH_3)_2S$) was measured from ND to 2.6 ppb. Considering the prevailing wind direction and air velocity ranging from 0.23 to 0.73 m/s within the boundary area, the odorous matters; NH_3, H_2S, CH_3SH, $(CH_3)_2S_2$ and $(CH_3)_2S$ were 0.2 to 4.5 ppm, 0.01 to 0.06 ppb, ND for$(CH_3)_2S$, respectively. These findings suggested that the odor compound, $(CH_3)_2S_2$, had the lowest detection level in the boundary area whilst $(CH_3)_2S$ cannot be detected within a 20-meter distance only. However, with these results, other odor compounds from pig buildings has to be further investigated under more controlled environmental factors.

Introduction

Nowadays, there has been an increase in intensive farming resulting to increased concentration of malodors. Consequently, numerous researches have been done to reduce malodors. For efficient reduction of malodors from livestock facilities, elimination of odor causing compounds should be given priority. Another important aspect of livestock waste management is the extent to which these malodors can be detected at a certain distant from the pig barn. This is equally important to determine also the stability or persistency of the odorous nature of the malodorants.

The distance from the pig barn to the nearest neighbor is critical in minimizing air quality impacts, such that the closer the neighbor, the more important odor control efforts become (ISU, 2004).

Methodology

There were 16 farms, with size ranging from small to large scale operation. The building length ranged from 4 to 45 meters while the width ranged from 9.7 to 43 meters. The manure treatment strategies were described including the ventilation types. The pig house facilities were gestating and breeding, nursery and growing houses. The air velocity was also measured to serve as a variable for standardizing the possible transit characteristics of the varying odor compounds. The malodorants were trapped using a handy gas sampler (Gastec GV-100,Shimoto, HS-7) Fig.1, equipped with a collection bag unit. Malodorants were detected using Gas Chromatography. The carrier gas wa He with inlet temperature at 150 ℃ (Split ratio 10:1), Column : HP-1 (30 m * 0.32 mm * 4 um), Column flow : 2.4 ml/min, Oven temp. : 40 ℃(2 min)-10 ℃/min-160 ℃(5 min), Detector : SCD(Temp. : 800 ℃, H2 : 100 ml/min, Air : 40 ml/min).

Results and Discussion

During the time of collection, the environmental conditions in the varying pig farms are presented in Table 1. Air velocity ranged from 0.09 to 0.73 m/s with the boundary area usually having the highest velocity. As expected the temperature outside in the boundary areas were slightly lower than the inside temperature of the different piggery house sections. Relative humidity was quite high in one boundary area at 90% while the other was only 69%.

Figure 1. The portable gas sampler

As presented in Table 2, the nursery section had the highest concentration of NH_3 emission at 6.68 mg/m^3, which could apparently be attributed to the high protein diet of the piglets. Temperature inside the nursery houses are also higher as compared to the other sections of the piggery house. This could be one factor for the variation. There was a heavy concentration of H_2S in the gestation and breeding section at 2,841.73 μg/m^3 . The massive concentration of feces of the sows and the contamination with the high protein diet of the sucklings could have resulted to high emission of this odor matter. methylmercaptan $(CH_3)SH$ were detected to be almost similar in emission levels from all the piggery sections while dimethylsulphide $(CH_3)_2S$ was maximized in the nursery section.

Table 1. Environmental conditions from the source of odor matter

Item*	Pig house	Air velocity (m/s)	Inside Temperature (□)	Relative-Humidity (%)
L	Gestation & breeding	0.20	25.0	84
	Farrowing	0.18	26.0	77
	Nursery	0.09	27.0	84
	Growing□finishing	0.24	25.0	83
	Boundary area	0.23	23.0	90
M-1	Gestation & breeding	0.22	22.0	75
	Farrowing	0.09	21.3	75
	Nursery	0.13	25.2	82
	Growing-finishing	1.11	21.3	81
M-2	Gestation & breeding	0.15	-	-
	Farrowing	0.33	28.6	71
	Nursery	0.19	-	-
	Growing-finishing(sawdust)	0.15	30.0	84
	Growing□finishing(slurry)	0.33	29.0	82
S	Gestation & breeding	0.10	25.0	74
	Farrowing	0.70	26.0	73
	Nursery	0.23	25.0	82
	Growing□finishing(sawdust)	0.30	25.0	76
	Boundary area	0.73	25.0	69

Table 2. Concentration of odor matter emissions from pig sections

Item		Gestation & breeding	Farrowing	Nursery	Growing □ finishing
NH_3 (□/□)	Arithmetic mean	□3.19	2.66	6.68	4.71
	Range	1.59~5.08	1.29~4.63	0.68~15.94	1.14~8.58
H_2S (□/□)	Arithmetic mean	2,841.73	908.59	289.15	1,549.58
	Range	78.78~10,188.46	64.21~3,313.33	44.47~904.95	64.21~4,406.64
$(CH_3)SH$ (□/□)	Arithmetic mean	21.86	21.00	24.64	22.07
	Range	N D~23.79	20.79~21.21	21.00~27.64	20.57~24.00
$(CH_3)_2S$ (□/□)	Arithmetic mean	7.75	5.81	11.35	8.30
	Range	6.64~8.30	N D~ 8.30	8.58~14.12	N D~14.39
$(CH_3)_2S_2$ (□/□)	Arithmetic mean	9.23	9.23	9.65	5.46
	Range	9.23~9.65	8.81~9.65	8.81~10.91	N D~9.23

Ammonia (NH_3) and hydrogen sulfide (H_2S) are two major odorous gases emitted from animal operations (Xue and Chen, 1999). These gases are generated while manure undergoes microbial degradation. Ammonia is produced by the decomposition of nitrogen-containing compounds in the excreta, especially in urine.

In Table 3, against the prevailing wind direction and air velocity ranging from 0.23 – 0.73 m/s within a 20-m boundary area, the odor matters namely; $NH_{3,}$ H_2S, $(CH_3)SH$), ($(CH_3)_2S$) and $(CH_3)_2S_2$) were substantially reduced to 0.15~3.42□/□, 20.34~104.43□/□, ND~21.00□/□, ND~9.65□/□ and ND for.$(CH_3)_2S_2$, respectively. Likewise the, reduction rates for the odor matters in the same order were; 78.24%, 76.61%, 24.02%, 32.94% and 100 %, respectively. These findings also suggested that the methylmercaptan $(CH_3)SH$ was highly concentrated and stable as it was still strongly detected as evidenced by its low reduction rate in the boundary area whilst dimethyldisulphide$(CH_3)_2S$ was the first odorant to be eliminated because of its zero detection level within a 20-meter distance only. Finally, dissipation of odorants from pig buildings has no relationship to their respective molecular weights but has to be further investigated under more controlled environmental factors.

Table 3. Concentration of odor matters in boundary area

Item	L	M-2	S
NH_3(□/□)	2.13	3.42	0.15
H_2S(□/□)	104.43	49.03	20.34
$(CH_3)SH$(□/□)	21.00	N D	20.79
$(CH_3)_2S$(□/□)	N D	N D	N D
$(CH_3)_2S_2$(□/□)	9.65	N D	8.39

Conclusion

Detection of odor matters within boundary areas remains a critical challenge to environmentalists as they are governed by several factors. The information in this field survey will therefore serve as a basis for devising scientific approaches to accurately quantify odor matters and recommend appropriate measures to mitigate their emission.

References

ISU.2004. Odor control methods used by Iowa pork producers. Iowa State University. University Extension Brochure.

Xue, S. K. and S. Chen. 1999. Surface oxidation for reducing ammonia and hydrogen sulfide emission from dairy manure storage. Transactions of ASAE. Vol. 42. No. 5. 1401-1408.

The Effects of Coordinate Rotation Procedure on Eddy Covariance and Relaxed Eddy Accumulation Flux Measurements

K. A. Baum and J. M. Ham
Kansas State University, Manhattan, Kansas

Abstract

Quantifying the exchange of traces gases between the atmosphere and agricultural operations (crop or animal) is crucial for advancing research on agricultural air quality. Micrometeorological techniques such as eddy covariance, relaxed eddy accumulation (REA), and the modified Bowen ratio are the most direct, unintrusive methods for measuring surface atmosphere exchange. All of theses techniques rely on three-dimensional sonic anemometry. Data from a sonic anemometer and the fluxes calculated from the results are subject to a mathematical processing step known as coordinate rotation before the fluxes can be interpreted. The objective of this research was to evaluate the two most widely used rotational schemes: (1) rotation to the natural wind coordinate (NWC), and (2) rotation using the planer fit method (PF). The traditional NWC procedure is a double or triple rotation procedure that aligns the mean wind direction with the x-axis and sets the cross-stream stress to zero every observational period. The PF method determines the same rotational angles by defining a three-dimensional 'plane' using historical three-dimensional wind data. Eddy covariance systems consisting of a sonic anemometer and a fast response open-path gas analyzer were deployed at 3-m above the soil surface at different locations in Kansas representing three different land/cattle management schemes: an ungrazed prairie, a grazed prairie, and two cattle feedlots. The effects of coordinate rotation were examined by comparing sensible heat, latent heat, and carbon dioxide fluxes using the two different rotation procedures. Additional work was conducted to examine the effect of rotation schemes on the measurement of ammonia fluxes when using REA. The differences between these two methods could be very important for estimating nutrient balances and calculating emission factors.

Ammonia Emissions from the Application of Dairy Effluent

M. Beene C. Krauter, and D. Goorahoo

California State University, Fresno
CSU, Fresno – Plant Science Department
CSU, Fresno – Center for Irrigation Technology

Abstract

The San Joaquin Valley (SJV), in the interior portion of California, is one of the most productive agricultural regions in the world where most of the state's 5 billion dollar dairy industry is located. Because of the its extent and continuing growth, agiculture is the major source of ammonia (NH_3) in California with dairies accounting for roughly 60% of statewide NH_3 emissions. Ammonia is of concern because of it's participation as a precursor to $PM_{2.5}$ as well as the passage of California State Bill 700 which has brought increased scrutiny to NH_3 emissions. The SJV experiences elevated levels of $PM_{2.5}$ usually in winter months. The dominant manure management practice at the dairies is a free stall flush system where water is flushed through barns where animals are housed and fed removing manure and depositing it eventually to a lagoon or storage pond. The effluent is applied several times a year through irrigation systems to surrounding crop land as a means of applying nutrients, water, and disposal of effluent. Dairy producers and agronomist are currently working to develop nutrient mangement plans to apply agronomic rates of nutrients while achieving maxium crop yields of forages. Losses of nitrogen occur through the volatilization of NH_3 from the application of dairy effluent. In order to develop accurated nutrient management plans these losses must be quantified.

Because free stall flush manure management systems are not common throughout the national dairy industry little research has been conducted on NH_3 emissions from these systems. Preliminary NH_3 emissions data from dairy manure applications was collected in the winter of 2005/2006 for a project to calibrate a computer simulation model of carbon and nitrogen biogeochemistry for California dairy systems. As part of this project emissions of NH_3 and nitrous oxide (N_2O) will be monitored from California dairy cropping systems focusing on manure applications.

NH_3 emissions were monitored form two manure appication methods in January and February 2006. A slurry injection method was monitored along with a more traditional application of effluent through flood irrigation. The injection of dairy slurry is rare with less than six producers known to use this practice in the state. Ammonia emissions were monitored using a USEPA Emission Isolation Flux Chamber. Samples were collected with active chemical filter packs consisting of 47mm glass microfibre filters treated with citric acid (3% in 95% Ethanol). The ammonium citrate was extracted from the filter with de-ionized water and analyzed with Nessler's Reagent and a spectrophotometer. Air was pulled out of the flux chamber with a personal air sampling pump at a flow rate of 2.0 L min^{-1} to sampling media for 15 to 25 minutes. Ultra zero air was used to flush chamber at a flow rate of 5.0 L min^{-1} for thirty minutes. Fluxes were calculated with formulas provided in the Measurement of Gaseous Emissions Rates from Land Surfaces Using an Emission Isolation Flux Chamber User's Guide.

Slurry injections were monitored two dates post-application, immediately and one week. Flux chambers were placed at the same undisturbed locations for the one week post-application samples. Three types of surface characteristics sampled by the flux chamber were evaluated, representing 25, 50, and 75% manure coverage of area, respectively . Percent total solids (TS) of slurry was 11% while the liquid effluent was estimated to be approximately 1 to 2 % TS. Ammonia emissions from the flood irrigation application of liquid effluent to a fallow field was sampled two and four weeks post-application. Two different surfaces were evaluated to characterize emissions, presence of solids and no solids on the surface of the field. All sampling was conducted from 9:30 to 16:00. Ambient temperatures ranged from 10 to 16 °C.

Ammonia fluxes from the slurry injection ranged from 1.2 to 352.1 $\mu g\ NH_3\text{-}N\ m^{-2}\ min^{-1}$ The highest 352.1 $\mu g\ NH_3\text{-}N\ m^{-2}\ min^{-1}$flux from the slurry injection occurred at 30 minutes post injection, at a location where 75% of the flux chamber area was covered with manure. Surface coverage of slurry seemed to be positively correlated with ammonia fluxes. The 25% manure surface area was determined to be most

representative of the total field from on site observations and consultation with the farm manager. Soil moisture conditions may have increased the surface area of the field covered with slurry as higher than normal levels of moisture did not allow for efficient injection. Emissions of ammonia at the 25, 50, and 75% manure coverage locations decreased by 99, 87, and 65% of initial fluxes sampled immediately post-application.

Ammonia fluxes from the liquid effluent flood irrigation application ranged from 4.4 to 116.9 µg NH_3-N m^{-2} min^{-1}. Fluxes of ammonia were generally higher at the head end of the irrigation check where more solids have settled out compared to the tail end. From two weeks post-application to four weeks post-application fluxes decreased by over 90% at both locations. It is assumed that the period of highest emissions would be during and immediately post-application of the effluent which was not sampled. In order to better understand emissions characteristics from this type of application sampling must be done during this period as well as during night hours to characterize assumed diurnal variations in emissions.

Future sampling will be conducted during the Spring and Fall months which are the most common periods to apply dairy effluent in California between cropping rotations of winter forage and summer corn silage. Application of dry manure from scraped corrals or solids separation processes will be monitored in addition to the injection and liquid effluent flood applications.

Improved Temporal Resolution in Process Modelling of Nitrogen Trace Gas Emissions

J.D. Beuning[1] and B.J. Van Heyst[1]
[1]School of Engineering, University of Guelph, Guelph, ON, Canada N1G 2W1

Introduction

An emerging issue in Canada is how to better quantify agriculture's contributions to atmospheric warming and pollution contamination generated by nitrous oxide (N_2O) and ammonia (NH_3) emissions. Agricultural soil emissions have far-reaching environmental impacts including stratospheric ozone destruction, global warming, ecosystem degradation, and contributions to secondary organic aerosol production causing adverse human health effects. Emission inventories are essential to predicting these emissions and their subsequent atmospheric transportation, transformation, and deposition. These inventories can also predict longer term trends and assess emission reduction strategies. The processes of soil N transformations and transport are complex because they are controlled by site specific factors (i.e. soil temperature, acidity, etc.) influenced by weather, vegetation, soil properties, and land management. Due to the high spatial and temporal variability associated with these processes, measurement-based emission inventories become expensive and emission factors can lose accuracy. Process-based models are capable of developing emission factors that account for the complex soil interactions, but current models lack temporal refinement in that they operate on a daily time step and few models consider NH_3 emissions.

Proposed model

The proposed model, AGRIN, seeks to develop a one-dimensional (vertical), time-dependent process model that predicts hourly N trace gas emissions from N applied to a bare soil in a northeastern Ontario climate. The model takes existing model theory (e.g. Molina et al. 1983; Parton et al. 1987; Hansen et al. 1990; Li et al. 1992) and experimental observations (e.g. Blagodatsky and Richter 1998; Reth et al. 2004) and develops a more refined temporal scale. The major N processes simulated include decomposition, volatilization, nitrification, denitrification, and leaching. See Figure 1 for a schematic of the model.

The soil module determines the soil heat and moisture environment which drives the rest of the modules. The decomposition module simulates the carbon and nitrogen flows through the soil organic matter pools to determine net mineralization of nitrogen. The nitrification module simulates nitrifier dynamics which control the oxidation of ammonium to nitrate while the denitrification module simulates denitrifier dynamics which control nitrate reduction to dinitrogen. Substrate allocation to each of the nitrification and denitrification modules is based on DNDC's "anaerobic balloon" (Li, 2000). N profiles are generated and the atmospheric transport module uses the surface concentrations to simulate N trace gas volatilization by applying a resistance analogy. General limitations of the model are that it's one-dimensional and does not incorporate the snowmelt or the influence freeze / thaw cycle(s) experienced in colder climates.

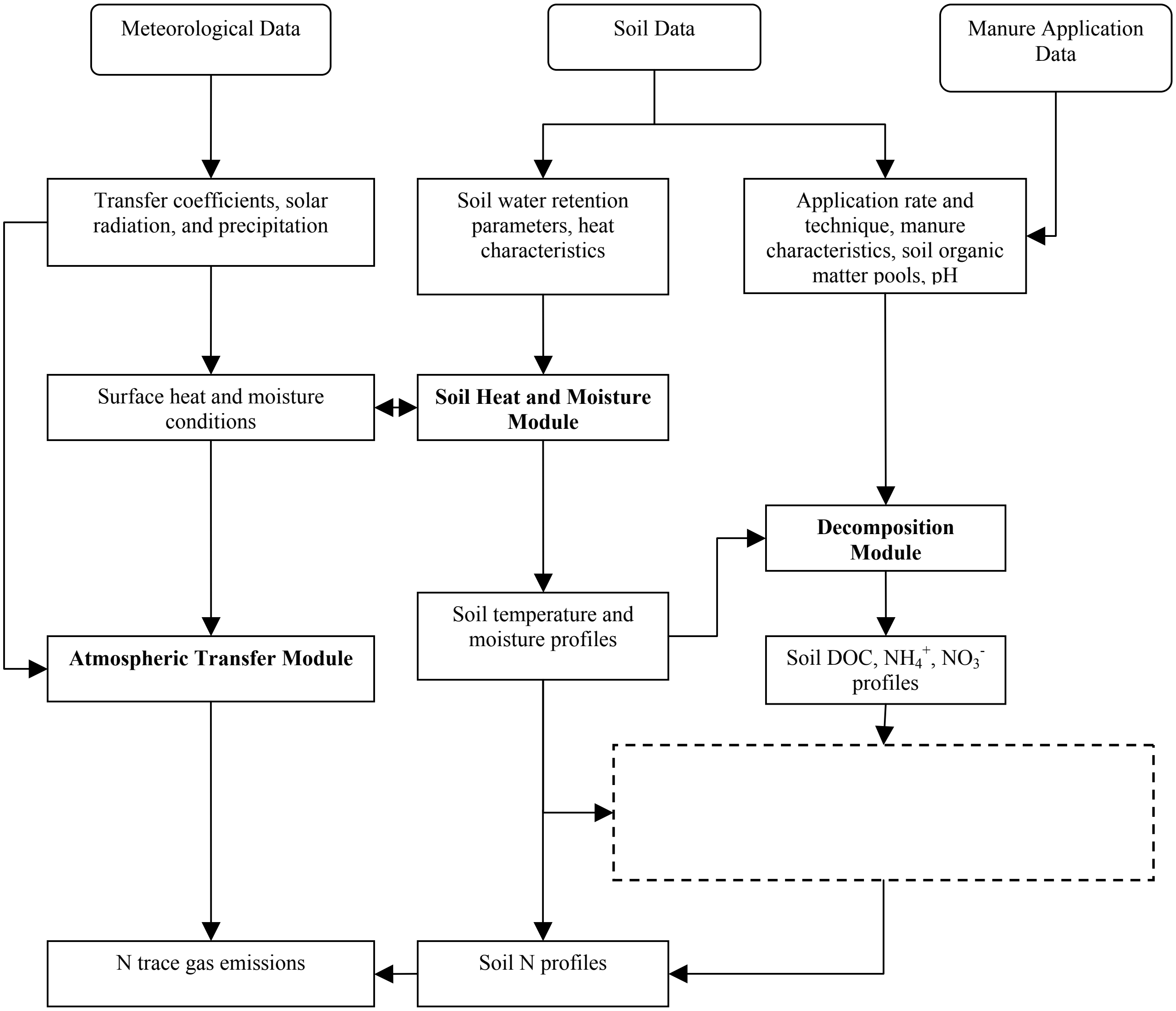


Figure 1: Schematic of AGRIN Model

The N species (organic N, NO_3^-, NO_2^-, NH_4^+, NH_3, N_2O, NO, N_2) profiles are calculated by applying a partial differential equation describing convective-dispersive movement through the soil:

$$\frac{\partial(C_s + \theta C_w)}{\partial t} = -\frac{\partial}{\partial z}\left[-\theta D \frac{\partial C_w}{\partial z} + q_w C_w\right] + S$$

where C_s is the adsorbed concentration of the species, θ is the soil volumetric moisture content, C_w is the concentration of the species in the soil solution, t is time, D is the diffusion coefficient of the species in soil, z is the depth below the soil surface, q_w is the soil water flux density and S is the source-sink term. The system of equations formed is solved numerically with the Crank-Nicholson finite difference scheme where the time derivatives are determined at the mid-point of a time step. The time step is user-specified and can be constant or dependent on convergence.

Experimental Study

A dataset was developed for model testing in August of 2005 when experiments were performed by Agriculture and Agri-Food Canada in Ottawa, Ontario. The experiments measured N_2O and NH_3 emissions following application of poultry manure and pig slurry to a bare field. Measurement techniques included flux gradient, relaxed-eddy accumulation and tunable diode laser. Ancillary measurements included soil properties, manure properties and hourly meteorological data.

Future Plans

Testing thus far has consisted mainly of soil module validation. Model calibration of the N modules is currently underway while validation of these modules will be conducted using the August 2005 dataset. Trends expected include large emissions occurring during application and subsequent emission trends associated with diurnal patterns. The goal of the model testing is to derive emission factors for N trace gases from an agricultural bare soil on a diurnal, monthly, and seasonal scale. Potential exists for the model to become a useful tool in predicting emissions on local, regional, or national scales. Other long-term objectives include generating input for short- and long-range transport models as well as to determine and assess emission reduction measures.

References

Blagodatsky, S.A. and O. Richter. 1998. Microbial growth in soil and nitrogen turnover: a theoretical model considering the activity state of microorganisms. *Soil Biology and Biochemistry* 30(13): 1743-1755.

Hansen, S., H.E. Jensen, N.E. Nielsen, and H. Svendsen. 1990. DAISY – Soil Plant Atmosphere Model. NPO Report No. A10. The National Agency for Environmental Protection, Copenhagen, 272 pp.

Li, C., S. Frolking, and T.A. Frolking. 1992. A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *Journal of Geophysical Research* 97: 9759-9776.

Li, C. and J. Aber. 2000. A process-oriented model of N2O and NO emissions from forest soils: 1. Model development. *Journal of Geophysical Research* 105: 4369-4384.

Molina, J.A.E., C.E. Clapp, M.J. Shaffer, F.W. Chichester, and W.E. Larson. 1983. NCSOIL, a model of nitrogen and carbon transformations in soil: description, calibration, and behavior. *Soil Science Society of America Journal* 47: 85-91.

Parton, W.J., D.S. Schimel, C.V. Cole, and D.S. Ojima. 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Science Society of America Journal* 51: 1173-1179.

Reth, S., K. Hentschel, M. Drosler, and E. Falge. 2004. DenNit – Experimental analysis and modelling of soil N2O efflux in response on changes of soil water content, soil temperature, soil pH, nutrient availability and the time after rain event. *Plant and Soil* 272: 349-363.

Effects of Acidifying Liquid Cattle Manure with Nitric or Lactic Acid on Gaseous Emissions

W. Berg[1], M. Türk[2] and H. J. Hellebrand[1]

[1]Department of Technology Assessment and Substance Cycles
[2]Department of Engineering for Livestock Management
Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB), Max-Eyth-Allee 100,
D-14469 Potsdam, Germany

Abstract

Animal manure is a source of undesired gaseous emissions as there are ammonia (NH_3), methane (CH_4) and nitrous oxide (N_2O). They can be reduced by manure additives. Investigations were done on acidifying liquid cattle manure with nitric or lactic acid respectively on laboratory scale. The manure was stored in open vessels with 50 kg for 92 days (nitric acid) and with 75 kg for 190 days (lactic acid), respectively.

Ammonia emissions could be reduced effectively with nitric acid as well as with lactic acid. About 70% of NH_3 emissions could be avoided. Lactic acid had a better abatement effect on methane emissions than nitric acid, the reduction rates were 90 and 75% respectively. Nearly no nitrous oxide was detected from the manure acidified with lactic acid. Whereas the manure acidified with nitric acid emitted a large amount of N_2O. Nitric acid is not an advisable emission abatement technique.

Introduction

Agricultural operations are a source of gaseous emissions. International notes and regulations aim at the reduction of NH_3 as well as green house gas emissions (UN/ECE, 1999; EU, 2001). Animal husbandry and manure management is the main anthropogenic source for NH_3 (Berg et al., 2003) and emits also CH_4 at a large extent (Mikaloff Fletcher et al., 2004). N_2O emissions have their main source in soil (Bouwman, 1990). Under special conditions only when surface is dry and encrusted, manure emits N_2O at a noticeable extent (Berg & Hörnig, 1997).

Emissions from manure can be reduced by additives. Manipulating the balance between ammonia (NH_3) and ammonium (NH_4^+) by lowering the pH value of the manure is a promising possibility to reduce not only NH_3 but also CH_4 emission. A direct influence of the pH value on N_2O emission is not known. The effects of two different acids on the mentioned gaseous emissions from liquid cattle manure are investigated.

Methodology

Investigations on acidifying liquid cattle manure were carried out on laboratory scale at the Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB) (Fig. 1). Two trials were done: trial I with lactic acid and trial II using nitic acid. Fresh liquid cattle manure was collected from a manure pit in a commercial dairy cattle house.

In trial I 75 kg liquid manure were stored in cylindric vessels for a period of 190 days. Vessels made of plexiglas® with a volume of 92.4 l (diameter and height 0.49 m respectively) were used. The manure was acidified with different amounts of lactic acid achieving a pH value of the liquid manure of 3.8, 4.3 and 4.8 respectively at the beginning of the storage period.

In trial II nitric acid and different vessles were used. The vessels were also made of plexiglas® but with a volume of 65.4 l and different shape (diameter 0.29 m, height 0.99 m). 50 kg liquid manure were stored in these vessels for a period of 92 days. The same pH values of the liquid manure were adjusted at the beginning of the investigations (3.8, 4.3 and 4.8).

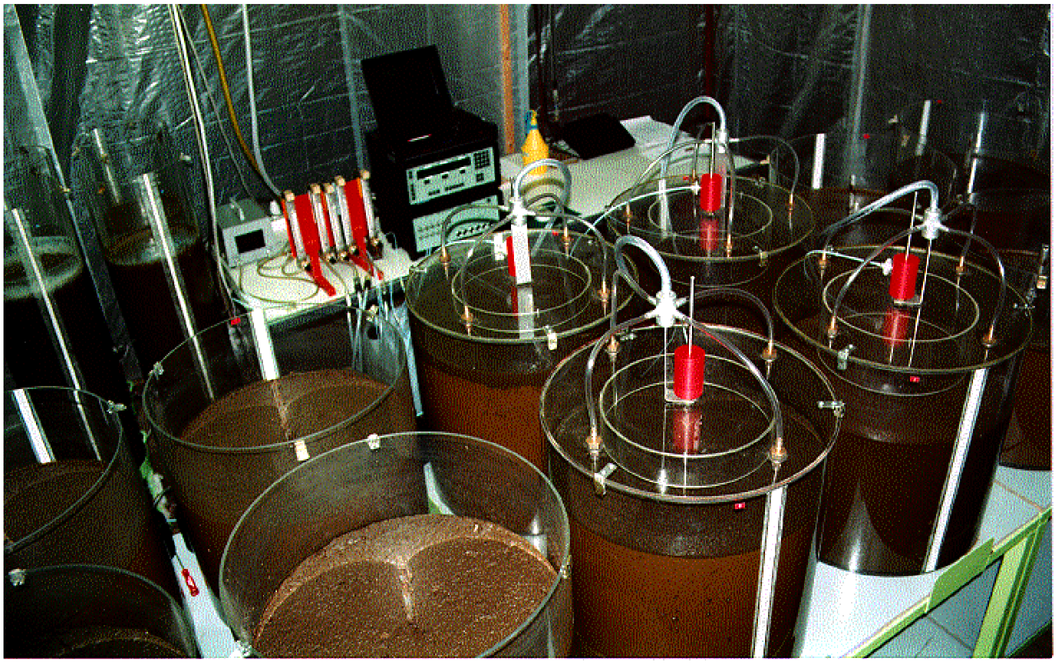


Figure 1. Experimental equipment for investigation of gaseous emissions as well as storage behavior.

Gaseous emissions were determined by using the open / dynamic chamber method. Vessels were closed and ventilated only during the measurements of the gaseous emissions with lids provided with air inlet and outlet. A compressor supplied the air inlets with fresh air. The fresh air flow rates were adjusted by air flow meters so that the air in the headspace was changed always one time per minute.

The headspace concentrations of the gases were determined by sampling exhaust air from each vessel and analyzing by a photoacoustic IR analyzer (multigas monitor). Ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2) and water vapor (H_2O) concentrations were measured in the headspace and in the fresh air. Headspace concentrations of the different vessels fresh air (background) concentrations deducted were compared with each other and the control within the trials respectively. The gas fluxes calculated from the concentrations could not be used for calculating fluxes from on-farm storage facilities. The different environment and volume to surface ratio of the vessels in the lab and on farms cause different gas fluxes.

The procedure of the measurement of the gaseous concentrations was the following: Exhaust air from each vessel headspace and fresh air were sampled sequentially at 20 minutes intervals. The first 16 minutes vessel exhaust air and the last 4 minutes fresh air was sampled. It took the photoacoustic IR analyzer 2 minutes for analyzing one sample. Thus 8 values for exhaust air were generated per vessel and 2 values for fresh air between each vessel. The first 5 values from vessel exhaust air were used for stabilization and the last 3 values for calculating a mean value representative for the measurement respectively. Fresh air between the vessels flushed the measuring chamber of the analyzer and demarcated measurements between each vessel. Fresh air concentrations were determined before and after the measurements of the first and the last vessel respectively.

Further parameters were determined:

- dry matter (DM), organic dry matter (oDM), total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN) and organic acids of the manure by chemical analysis at the beginning and the end of the investigation period and between
- manure temperature and pH value
- sedimentation
- flow properties of the liquide manure by a rotational-type viscometer.

Results and Discussion

Manure Property

Properties of manure before and after storage are presented in table 1. The dry matter content of the manure was 7.8 and 8.0% at the beginning and 11.0 and 7.7% at the end of the storage period for trial I (lactic acid) and trial II (nitric acid) respectively. The long storage period of 190 days and the small volume to surface ratio of 0.398 of the vessels in trial I caused the noticeable increase of the dry matter content.

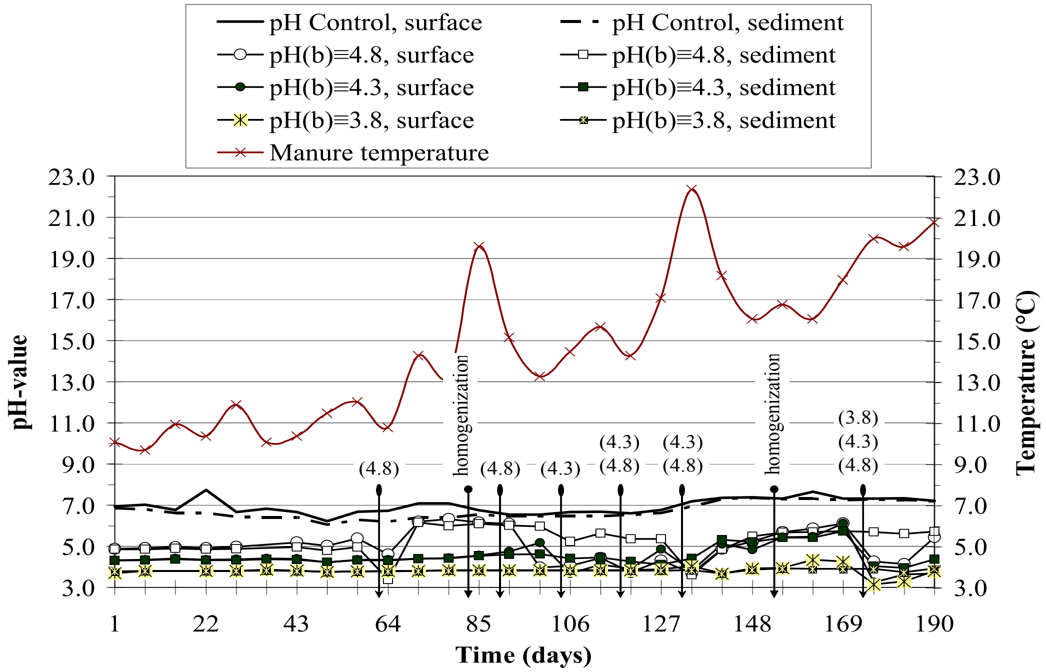
Table 1. Contents of total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) of the manure samples before and after storage.

	TKN (g N kg-1 fresh mass)		TAN (g N kg-1 fresh mass)	
	Beginning	End	Beginning	End
Control, lactic acid	3.06	3.03	1.31	0.98
PH(b)≡4.8, lactic acid	3.02	3.58	1.29	1.53
PH(b)≡4.3, lactic acid	3.10	3.75	1.28	1.56
PH(b)≡3.8, lactic acid	2.88	3.67	1.24	1.56
Control, nitric acid	3.02	3.00	1.17	1.33
PH(b)≡4.8, nitric acid	3.35	3.23	1.19	1.27
PH(b)≡4.3, nitric acid	3.51	3.28	1.17	1.12
PH(b)≡3.8, nitric acid	3.55	3.41	1.17	1.16

Approximately 2, 4 or6% by volume of 50% concentrated lactic acid were necessary to lower the pH value of the liquid cattle manure to 5, 4.5 or 4.0. Nitric acid was much more effective, only 1, 1.3 and 1.5% by volume of 50% concentrated acid were needed to achieve the same pH values mentioned before.

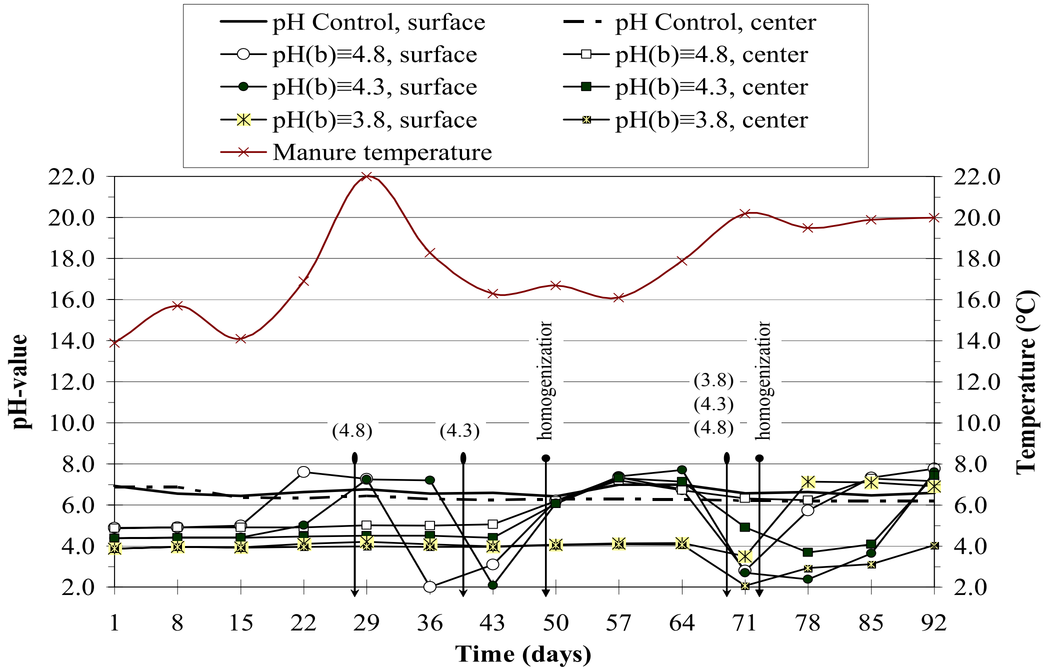
The courses of manure pH values and temperatures are shown in figures 2 and 3. Lower pH values were more steady than higher ones. During trial I (Fig. 2), it was noted that in order to maintain desired pH values, lactic acid had to be added several times, at day 63 (pH(b)≡4.8), 91 (pH(b)≡4.8), 104 (pH(b)≡4.3), 119 (pH(b)≡4.8, pH(b)≡4.3), 133 (pH(b)≡4.8, pH(b)≡4.3) and 174 (all). All samples were homogenized two times, at day 84 and 154. Nitric acid was added three times during trial II (Fig. 3). Homogenizations of all samples were carried out also two times, at day 49 and 72. The mean pH values of the manure are given in table 2.

Manure temperatures were increasing in the course of the investigation period due to increasing room temperature. The range was between 10 and 22°C. Trial II began at day 75 of trial I. Thus in the following the course of the manure temperatures were nearly identically for both trials.



(3.8) (4.3) (4.8) − lactic acid added to sample pH(b)≡3.8, 4.3, 4.8 respectively

Figure 2. pH values and temperature of the lactic acid added liquid cattle manure.



(3.8) (4.3) (4.8) − nitric acid added to sample pH(b)≡3.8, 4.3, 4.8 respectively

Figure 3. pH values and temperature of the nitric acid added liquid cattle manure.

Table 2. Mean pH values of the manure samples.

	pH
Control, lactic acid	6.50
pH(b)≡4.8, lactic acid	5.73
pH(b)≡4.3, lactic acid	5.14
pH(b)≡3.8, lactic acid	4.18
Control, nitric acid	6.85
pH(b)≡4.8, nitric acid	5.20
pH(b)≡4.3, nitric acid	4.49
pH(b)≡3.8, nitric acid	3.86

Ammonia Emission

NH_3 emissions were proportional to manure pH values. Lactic acid reduced NH_3 emission much more effective than nitric acid. With mean pH values of 5.73, 5.14 and 4.18 (Tab. 2) lactic acid reduced NH_3 emissions by 65, 72 and 88% respectively. Whereas nitric acid could reduce emissions with lower mean pH values of 5.20, 4.49 only by 29, 49 and 71% (Tab. 3).

Table 3. Mean ammonia (NH_3) emissions of the manure samples.

	Headspace concentration ($mg\ m^{-3}$)	Emission rate ($g\ m^{-2}\ d^{-1}$)	($g\ m^{-3}\ d^{-1}$)
Control, lactic acid	7.00	0.89	2.49
pH(b)≡4.8, lactic acid	2.43	0.31	0.90
pH(b)≡4.3, lactic acid	1.96	0.25	0.71
pH(b)≡3.8, lactic acid	0.85	0.11	0.31
Control, nitric acid	9.55	2.78	3.67
pH(b)≡4.8, nitric acid	6.79	1.96	2.61
pH(b)≡4.3, nitric acid	4.83	1.40	1.85
pH(b)≡3.8, nitric acid	2.76	0.80	1.06

Nitrous Oxide Emission

A slightly N_2O emission was detected from the control of trial I when it was getting dry and encrusted (Tab. 4). When the crust was destroyed by homogenization no N_2O emission occurred. But in the course of the following weeks this process started up again and N_2O was increasing again.

Manure acidified with nitric acid emitted N_2O at a large extent, although the manure surface nearly did not became encrusted. At the samples with higher pH values higher emission rates were measured than at the samples with lower pH values. Adding acid again and homogenizations did not prevented denitrification processes effectually but stimulated them.

Table 4. Mean nitrous oxide (N_2O) emissions of the manure samples.

	Headspace concentration ($mg\ m^{-3}$)	Emission rate ($g\ m^{-2}\ d^{-1}$)	($g\ m^{-3}\ d^{-1}$)
Control, lactic acid	0.49	0.062	0.174
pH(b)≡4.8, lactic acid	0.05	0.006	0.019
pH(b)≡4.3, lactic acid	0.04	0.005	0.014
pH(b)≡3.8, lactic acid	0.02	0.003	0.007
Control, nitric acid	0.0	0.0	0.0
pH(b)≡4.8, nitric acid	14.0	4.07	5.38
pH(b)≡4.3, nitric acid	12.5	3.62	4.78
pH(b)≡3.8, nitric acid	7.6	2.21	2.92

Methane Emissions

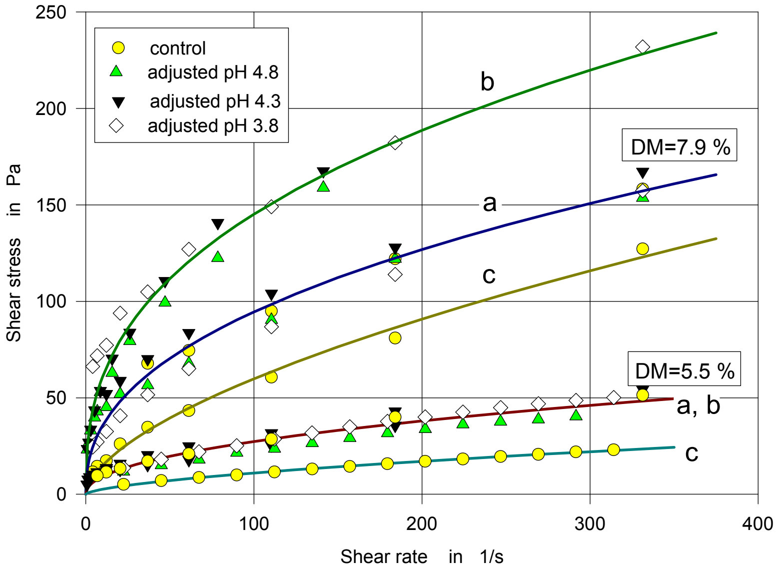
Lowering manure pH generally reduced CH_4 emission. Also here lactic acid was much more effective than nitric acid. From the samples acidified with lactic acid nearly no CH_4 emitted (reduction rates of 94, 91 and 98%). Whereas nitric acid could reduce emissions with lower mean pH values of 5.20, 4.49 (Tab. 2) only by 17, 64 and 75% (Tab. 5).

Table 5. Mean methane (CH_4) emissions of the manure samples.

	Headspace concentration (mg m^{-3})	Emission rate	
		(g m^{-2} d^{-1})	(g m^{-3} d^{-1})
Control, lactic acid	53.8	6.84	19.1
pH(b)≡4.8, lactic acid	3.18	0.41	1.18
pH(b)≡4.3, lactic acid	4.59	0.58	1.67
pH(b)≡3.8, lactic acid	1.03	0.13	0.38
Control, nitric acid	7.90	2.30	3.03
pH(b)≡4.8, nitric acid	6.55	1.90	2.51
pH(b)≡4.3, nitric acid	2.87	0.83	1.10
pH(b)≡3.8, nitric acid	2.00	0.58	0.77

Rheological Property

At the beginning of the storage period there was only a slightly influence of acid addition on the flow properties of the manure. But after the storage period of 190 days, appreciable differences were measured. The flow properties of the untreated manure became better, whereas the acidified manure had a higher viscosity. It was caused by reduced conversion processes and a higher dry matter content.



a – control and acidified manure at the beginning of the storage period
b – manure with lactic acid at the end of the storage period
c – control at the end of the storage period

Figure 4. Flow curves of cattle slurry with lactic acid before and after storage

Conclusions

Adding nitric acid or lactic acid to liquid cattle manure gave different effects. Nitric acid could lower the pH value more efficiently. 1.3% by volume of 50% concentrated nitric acid were necessary to reach a manure pH of 4.5, whereas 3.7% by volume of 50% concentrated lactic acid were required to reach the same manure pH value. Advantages of lactic acid during acidifying were a considerably lower foam formation and a more innocuous handling than with nitric acid.

Both lactic and nitric acid could reduce ammonia emissions effectively, the reduction rate was nearly 90 and 70% respectively. In contrast, the effects on nitrous oxide and methane were quite different for both acids. From the manure acidified with lactic acid, nearly no nitrous oxide was detected, more than 90% of the methane emission could be detained. From the manure acidified with nitric acid, a large amount of nitrous oxide was emitted. The measured mean headspace concentration was about one order of magnitude higher than that of the control. The methane emission was about 25% of the control.

Ammonia emissions can be reduced effectively with nitric acid as well as with lactic acid. Lactic acid has a better abatement effect on methane emissions than nitric acid. Nitric acid is not an advisable emission abatement technique.

References

EU (European Union). 2001. Directive of the European Parliament and of the Council on National Emission Ceilings for certain Atmospheric Pollutants. Directive 2001/81/EC. 23. Oct.2001. www.europa.eu.int/eur-lex/pri/en/oj/dat/2001/l_309/l_30920011127en00220030.pdf (December 10, 2002)

Bouwman, A.F. (Ed.). 1990. Soils and the greenhouse effect. Chichester. John Wiley & Sons.

Berg, W. and G. Hörnig. 1997. Emission Reduction by Acidification of Slurry - Investigations and Assessment. International Symposium "Ammonia and Odour Control from Animal Production Facilities". Vinkeloord. The Netherlands. October 6–10, 1997. p. 459–466.

Berg, W., R. Brunsch, B. Eurich-Menden, H. Döhler, U. Dämmgen, B. Osterburg and A. Bergschmidt: Ammonia Emissions from German Animal Husbandry. 3rd International Conference on Air Pollution from Agricultural Operations. Raleigh. NC. USA. 12–15 October 2003. p. 131–138.

Mikaloff Fletcher, S.E., P.P. Tans, L.M. Bruhwiler, J.B. Miller and M. Heimann: CH_4 sources estimated from atmospheric observations of CH_4 and its $^{13}C//^{12}C$ isotopic ratios: 1. Inverse modeling of source processes. Glob. Biochem. Cycles, 18, GB4004, doi:10.1029/2004GB002223, 2004.

UN/ECE (United Nations Economic Commission for Europe). 1999. Protocol to the 1979 Convention on Long-rang Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground-level Ozone. 15.Oct. 1999. UN/ECE/EB.AIR/1999/1. www.unece.org/env/lrtap/protocol/99multi.htm (December 10, 2002)

Real-Time Monitoring of Air Pollution Due to Wildland Fires, Using a Mesoscale Model

Sanjeeb Bhoi and John J. Qu.

Center for Earth Observing and Space Research (CEOSR), School of Computational Sciences (SCS), George Mason University, Fairfax, VA 22030, USA

Abstract

In this paper a mesoscale model coupled with near real-time remote sensing data, has been applied to forecast air pollution due to wildland fires. Operational Multiscale Environment model with Grid Adaptivity (OMEGA) developed by SAIC (Science Applications International Corporation) is used in our current study. Satellite images have been used along with the NFDRS (National Fire Danger Rating) fuel load data to estimate the current fuel load available for burning. Emission from the fire has been calculated by estimating the area burned by the fire using real-time satellite data, and using emission factors given by EPA (Environmental Protection Agency). We have concentrated our efforts on estimating the emission of $PM_{2.5}$ and Carbon Monoxide due to wildland fires. A forest fire in the Eastern United States has been taken as a case study and the accuracy and efficiency of the model to run on real time basis has been shown. The whole processing is done using a sixteen node parallel cluster, so as to speed up the processing time for the model. A framework has been proposed to use mesoscale model along with real-time remote sending data to automatically detect fire pixels, run the model and generate the output in GIS (Geographic Information Systems) format to be distributed on the web. This will facilitate rapid distribution of forecast result which will be of immense help to persons involved in disaster management of wildland fires.

Carbon Dioxide Emissions from Agricultural Soils

P. Bielek

Soil Science and Conservation Research Institute, Bratislava, Slovak Republic

Abstract

Carbon dioxide emissions from soils of Slovakia have been determined and generalized. Absorption method of the CO_2 release determination from soil have been used. Data from 9 different soil places were collected during the three years and afterward processed and generalized.

About 10 061 thousand tons of C-CO_2 can be produced in average from agricultural soils of Slovakia during the growing season (245 days). It is about 4.2 tons C-CO_2 per 1 ha. Less productive soils release more CO_2 than high productive soils. Most of C-CO_2 is emitted from areas of Cambisols (3475 thousand tons), Fluvisols (1710 thousand tons) and Haplic Luvisols (1348 thousand tons).

Total amounts of C-CO_2 yearly released from agricultural soils of Slovakia is very close to the total C-CO_2 emissions by Slovakian industry.

Introduction

Energy and chemical substances are transformed in soils as essential soil functions in nature. Some incomes from those transformations in soil can be utilized by agriculture and another soil use practices. Mainly effects on air quality can be discussed. In this case is CO_2 released from soil into the air very important parameter of soils.

The CO_2 production in soil and consequently CO_2 emission from soil into the open air is a significant factor of air quality formation. Equilibrium between both CO_2 release from soil and CO_2 assimilation by plants can be considered as one of the most important principle of ecological stability of the nature.

Of coarse, a concrete data about CO_2 release from soil must be determined and presented if we want to evaluate some effects of soil on CO_2 contents in the open air. Accounting data of the CO_2 release from soil into the air are available from separate scientific and expert publications and from generalized (e.g. IPCC) studies. From national policies point of view also the data screening from different state territories must be available. This philosophy was adopted before our experimental activities.

Materials and Methods

In Table 1 contains data on the research sites (plots) and treatments used. For 3 years, the soils were sampled five times yearly in March, May, July, September, and November to a depth of 0.05 - 0.15 m. Non-N-fertilized treatments were used. Unified plant rotation was used in all plots (legumes, corn plants, and root crops with details depending on soil ecological conditions). The nitrification intensities in the soil samples and the CO_2 release intensities from soils were determined simultaneously by 14-days incubation tests.

Indexes of soil quality (productivity) were determined for each experimental site on the basis of soil ecological parameters by method of Dzatko et al. (1976). Indexes of soil quality can be determined for each site from Geographical Information System (GIS) database for Slovakian agricultural soils (productivity grades, 1 - 100). The indexes of productivity were identified for each experimental site to make a generalized data assessment.

Table 1: Soil types and treatments in the experimental plots

No	Soil type*	Treatments** N (-)
1	Cambisols	40/100
2	Plano-Gleyic Luvisols	170/300
3	Fluvi-Eutric Gleysols	40/110
4	Stagno-Gleyic Luvisols	40/100
5	Eutric Fluvisols	55/100
6	Calcaro-Haplic Chernozems	40/110
7	Fluvi Calcaric Phaeozems	6/110
8	Orthic Luvisols	90/100
9	Albo-Gleyic Luvisols	60/120

* According to WRB (1998) **; N (-): applied P_2O_5 and K_2O (kg ha^{-1}); N (+):

Results and Discussion

Carbon dioxide is produced by soil organisms through respiration. Therefore, the intensity of CO_2 release from soil was in the past considered as a "biological activity of soil". Now it is usually considered as data about carbon mineralization in soil. Moreover, sometimes the intensity of CO_2 release is simply called "loss of soil organic matter". From a greenhouse-effect point of view, this is a source of greenhouse gasses.

It is well known that the CO_2 release from soil can be in relatively large quantities (from hundreds of kilograms (C) to several tons per ha a year) (Glinski and Stepniewski 1985, Cole et al. 1990, Anderson 1995, Grant et al. 2002). From many published data it is clear that farming land produces more CO_2 than do other soils. Besides, manured soil can release more CO_2 than non-fertilized soil; drained soil, more than undrained soil; more productive soil, less than less productive soils; and so on (Richter 1974, De Jong 1981, Buyanovsky et al. 1986, Rochette et al. 1991, Reicosky and Lindstrom 1995).

This is a generalized overview, but specific data are very different under different soil conditions. CO_2 release is a very sensitive soil parameter with high variability from soil to soil and from land to land. When we want to have general data about CO_2 release from soils, we have to make detailed observations. This philosophy had been adopted before our relatively extended research and before all determinations of CO_2 emissions from soils were performed. The averaged data of CO_2 release from the soils investigated are collected in Table 3. Apart from soil types, the table also lists soil-production potentials in the form of indexes of soil productivity. It is clear from Table 2 that different soils show relatively deferent CO_2 release potentials (from about 30 to about 89 mg C-CO_2 kg^{-1} within 14 days). We can see that less-productive soils release more CO_2 than high-productive soils.

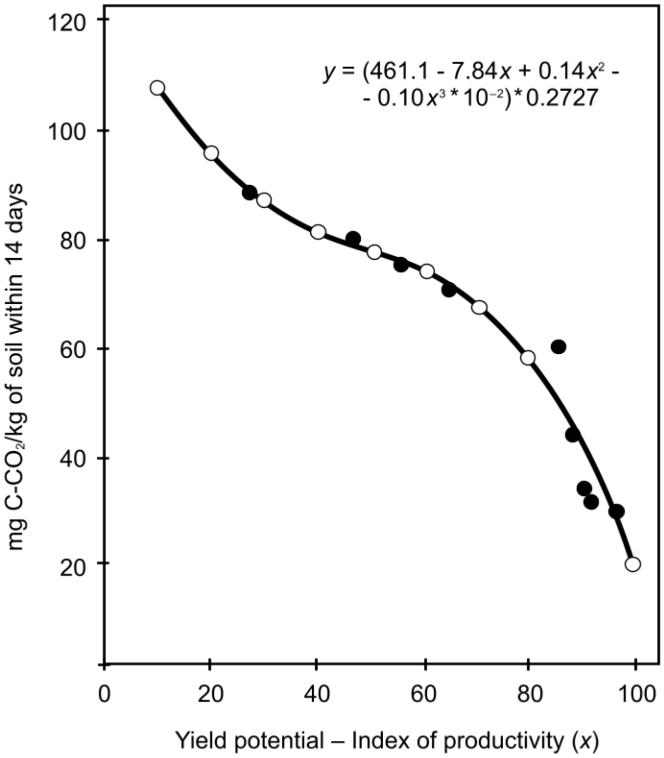
Table 2: CO_2 emissions from soils of experimental sites (non-fertilized plots)

Soil Type *	Index of soil productivity	mg C-CO_2 kg of soil
Eutric Cambisols	28	89
Luvic Stagnosols	47	80
Gleyic Eutric Fluvisols	55	75
Albic Stagni-Haplic Luvisols	64	72
Eutric Fluvisols	90	34
Calcaric Haplic Chernozems	91	31
Calcaric Mollic-Gleysols	95	30
Haplic Luvisols	85	61
Stagnic Glossisols	88	45

* WRB 1998

The regression between indexes of soil productivity and CO_2 release from soil is presented graphically in Figure 1. With this regression model, we calculated specific data for CO_2 release from the main soil units in Slovakian soil cover (Table 3). The last column of this table presents specific quantities of $CO_{2,}$ which could be released from specific areas of specific soil units in Slovakia (values calculated with the help of the GIS database for the agricultural soils of Slovakia).

Figure 1. CO_2 emission from soils in relation to soil yield potentials



It can be said that on the average, about 10,061 thousand tons of C-CO_2 can be produced in the soil cover (agricultural soils) in Slovakia during the growing season (about 4.2 tons of C-CO_2 per ha within the growing season). Most of C-CO_2 is emitted from Cambisols (3, 475 thousand tons), Fluvisols (1,710 thousand tons) and Haplic Luvisols (1,348 thousand tons). This is not only because of the high intensities of CO_2 release from these soils but also because of their widespread occurrence on the territory of Slovakia. The total C-CO_2 emission from the Slovakian industry was estimated to be about 11,700 thousand tons (Ministry of Environment 2004). This amount is very close to the natural CO_2 amount produced by soils.

Table 3: CO_2 emissions from different soils

*Soil type**	Index of soil productivity	mg C-CO_2 kg within 14 days	tons C-CO_2 ha^{-1} within growing season	C-CO_2 thousend tons from total area of soils within growing season
Fluvisols and Calcaric Fluvisols	34-95	86.4-33.4 (59.9)	3.78	1 710
Mollic Fluvisols and Calcaric Mollic Fluvisols	52-100	79.4-21.0 (50.2)	3.44	644
Calcaric Haplic Chernozems	67-96	71.8-31.0 (51.4)	3.52	525
Haplic Chernozems and Luvi-Haplic Chernozems	60-93	76.0-37.7 (56.8)	4.03	677
Haplic Luvisols and Albi-Haplic Luvisols	48-90	80.9-43.7 (62.3)	4.45	1 348
Albic Luvisols and Stagnic Glossisols	26-66	91.1-72.5 (81.8)	5.01	254
Planosols and Stagnosols	25-50	91.8-80.2 (86.0)	5.05	883
Cambisols and Umbrisols	15-50	101.3-80.2 (90.7)	4.95	3 475
Rendzic Leptosols	13-40	103.8-83.8 (93.8)	4.43	505
Podzols	3-10	119.6-107.9 (113.7)	5.17	15
Solonchaks and Solonetz	5-10	115.9-107.9 (111.9)	5.09	25

* WRB 1998

References

Anderson, D.V. 1995. Decomposition of organic matter and carbon emissions from soils. In: Lal E et al. (eds): *Soil and Global Change*. Lewis Publisher, Boca Raton, London, Tokyo: 165-175.

Buyanovsky, G.A., Wagner, G.H., Gantzer, C.J. 1986: Soil respiration in a winter wheat ecosystem. *Soil Sci Soc Am J*, 350, 338-344.

Cole, V.C., Burke, I.C., Parton, W.J., Schimel, D.S., Ogima, D.S., Stewart, J.W.B. 1989. Analysis of historical changes in soil fertility and organic matter level of the North American Great Plains. In: *Proc Soil and Crop Workshop*. Univ. Saskatchewan, Saskatoon, SK, p 1-10.

De Jong, E. 1981. Soil aeration as affected by slope position and negative cover. *Soil Sci* 131, 34-43.

Džatko, M., Hraško, J., Juráň, C., Linkeš, V. 1976. Metodika zatrieďovania poľnohospodárskych pôd SSR do bonitných tried. Project Report (Methods of soil productivity evaluation in Slovakia), Soil Science and Conservation Research Institute Bratislava.

Glinski, J., Stepniewski, W. 1985. Soil aeration and its role for plants. *CRC Press Inc. Boca Raton*, FL.

Grant, B. et al. 2002. Estimated N_2O and CO_2 emissions as influenced by agricultural practices in Canada. In: *Soil Organic Carbon and Agriculture*: Developing Indicators for Policy Analyses. Proceeding of an OECD Expert Meeting, Ottawa, Canada: 215-227.

Klinda, J. and Lieskovská, Z. 2004. Správa o stave životného prostredia v SR v roku 2004 (Environment Report of Slovakia, 2004). *Ministry of Environment of Slovakia*, 244 pp.

Reicosky, D.C., Lindstrom, M.J. 1995. Impact of fall tillage on shortterm carbon dioxide flux. In: Lal R. et al (eds): *Soil and Global Change*, 177-187.

Richter, J. 1974. A comparative study of soil gas regime in a soil tillage experiment with different soils. I. Field measurements. *Z Pflanzenernähr Bodenkd* 137, 135-147.

Rochette, P., Desjardins, R.L., Pattey, E. 1991. Spatial and temporal variability of soil respiration in agricultural fields. *Can J Soil Sci* 71, 189-196.

World Reference Base for Soil Resources (WRB) 1998. *ISRIC Wageningen*, 88 pp.

Measurement and Modeling of Hydrogen Sulfide Emissions Across the Gas-Liquid Interface of an Anaerobic Swine Waste Treatment Lagoon

J. Blunden[1], V.P. Aneja[1], and J.H. Overton[2]
[1]Box 8208 Jordan Hall, North Carolina State University
Department of Marine, Earth, and Atmospheric Sciences
Raleigh, NC 27695-8208, U.S.A.
[2]1911 Fountain Ridge Road, Chapel Hill, NC 27514

Abstract

Hydrogen sulfide (H_2S) is a colorless gas emitted during decomposition of hog manure that produces an offensive "rotten egg" smell and is considered a toxic manure gas. In the southeastern US, anaerobic waste treatment lagoons are widely used to store and treat hog excreta at commercial hog farms. Environmental concerns and complaints regarding air and water quality associated with the increased number of animals and management of subsequent wastes accompanying the growth of this industry has been considerable. However, due to a lack of intensive measurement initiatives, emissions of hydrogen sulfide from anaerobic waste treatment lagoons have not been well quantified.

Under anaerobic conditions, any excreted sulfur that is not in the form of H_2S (i.e., certain amino acids) will be reduced microbially to produce H_2S and so manures managed as liquids or slurries are potential sources of hydrogen sulfide emissions. The magnitude of H_2S emissions in this type of environment is a function of liquid phase concentration, temperature, pH and meteorological parameters. In aqueous form, H_2S exists in equilibrium with the bisulfide anion (HS^-) and sulfide anion (S^{2-}). Temperature and pH affect the solubility of H_2S in water. As pH shifts from alkaline to acidic ($pH<7$), the potential for H_2S emissions increases.

The process of hydrogen sulfide emissions from anaerobic waste treatment lagoons are investigated using a Coupled Mass Transfer with Chemical Reactions Model. This model is based on the concept of simultaneous mass transfer and equilibrium chemical reactions. Both aqueous phase and gas phase reactions are considered. A sensitivity analysis was performed and model results were compared with hydrogen sulfide fluxes measured at a commercial swine finishing farm waste treatment storage lagoon in North Carolina using a dynamic emission flux chamber system. The measurements were made continuously for ~5 day increments over all four seasons such that diurnal and seasonal variations were established. Experimental results will be utilized to evaluate the model's accuracy in calculating lagoon hydrogen sulfide emissions.

Introduction

Hydrogen sulfide is a colorless, potentially lethal gas released from swine manure (U.S.EPA, 2001). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). The U.S. Center for Disease Control (CDC) warns that brief exposures to concentrations greater than 500 ppm can cause unconsciousness or death (ATSDR, 2004). With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the primary gases released from swine facilities that is associated with odor complaints due to it's characteristic "rotten egg" smell.

Once released into the atmosphere, hydrogen sulfide reacts with the hydroxyl radical, OH, oxidizing to form sulfur dioxide (SO_2). Sulfur dioxide then undergoes a series of photochemical reactions, and may eventually form sulfuric acid (H_2SO_4). Such atmospheric gas phase reactions may lead to the formation of condensable products that associate with the atmospheric aerosol, e.g., gaseous H_2SO_4 may be neutralized by ammonia to form sulfate salts (Warneck, 2000). Aerosols such as ammonium sulfate may transport and deposit downwind of its source, possibly leading to nitrogen overloading and associated environmental problems such as enhanced eutrophication in sensitive river/coastal ecosystems and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

To date, few studies have reported H_2S emissions from waste storage treatment lagoons (Zahn et al., 2002; Lim et al., 2003). Arogo et al. (2000) studied the concentration and production of hydrogen sulfide from stored liquid in a laboratory experiment. Arogo et al. (1999) have investigated the effects of environmental parameters (wind speed and air temperature) and manure properties (solids content and liquid temperature) and developed a mass transfer coefficient for emission of hydrogen sulfide from liquid swine manure.

Over the last few years, changes in livestock production methods in the U.S. have led to the emergence of large-scale commercial livestock operations, substantially increasing the number of animals in geographically concentrated areas (Aneja et al., 2006). As emissions of trace gases (i.e., nitrogen and sulfur species) likely increase in parallel with the growth and consolidation of this industry, it is important to ensure that these operations do not exceed state regulatory levels for gases such as hydrogen sulfide.

In this study, a Coupled Mass Transfer and Chemical Reactions Model based on the concept of simultaneous mass transfer and equilibrium chemical reaction is used to predict the rates of hydrogen sulfide emission from swine waste storage and treatment lagoons. A field experiment was previously conducted at a commercial swine finishing operation in North Carolina. These experimental results, along with values reported in the literature, are used to evaluate the model's accuracy in calculating lagoon hydrogen sulfide emissions.

Model and Field Experimental Methods

Experimental Flux Measurements

Hydrogen sulfide flux measurements were made at a commercial swine finishing operation in eastern North Carolina. The waste from the animal confinement houses was flushed out with recycled lagoon effluent and discharged into the anaerobic lagoon from each house approximately once per week (varying days for each house).

Hydrogen sulfide flux was measured using a dynamic flow through chamber system (Aneja et al., 2000), consisting of a fluorinated ethylene propylene (FEP) Teflon-lined open bottom cylinder inserted into a floating platform. When the platform and chamber system were placed at a randomly chosen location on the lagoon, the chamber penetrated the lagoon surface to a depth of 6-7 cm, thus forming a seal between the lagoon surface and the air inside the chamber. Compressed zero-grade air was pumped through the chamber at a known flow rate and the air inside the chamber was continuously stirred by a motor driven Teflon impeller. Once the chamber reached steady-state conditions, samples were drawn through Teflon tubes to a Thermo Environmental Instruments (TEI) Model 450C pulsed fluorescence H_2S/SO_2 analyzer where the volumetric concentration was measured.

Continuous measurements were made for about a one-week period during four seasons, beginning October 2004 and ending June 2005, in order to determine seasonal trends. A Model CSIM11 pH probe and a CS107 temperature probe (Campbell Scientific Inc., Logan, UT) were submerged in the lagoon at a depth of ~6-7cm beneath the surface in order to continuously monitor near-surface lagoon pH and lagoon temperatures.

Lagoon Sample Collection

To determine the concentration of total sulfide samples in the slurry, liquid samples were collected from the lagoon surface 1-2 times per day during the flux experiment. Lagoon samples collected were preserved with 6N sodium hydroxide and 2N zinc acetate to pH > 9, according to North Carolina Division of Water Quality (NC DWQ) specifications.

Aqueous hydrogen sulfide exists in equilibrium with the hydrogen sulfide anion (HS^-) and the sulfide anion (S^{2-}) and all three comprise total sulfide. Once total sulfide (C_{TS}) concentration has been determined, the bulk dissolved hydrogen sulfide, which is a function of C_{TS}, pH, and lagoon temperature (T_L), can then be calculated. Snoeyink and Jenkins (1980) determined the relationship for the fraction of sulfide species (H_2S, HS^-, S^{2-}) present in aqueous solution as a function of pH and estimated the aqueous H_2S concentration for known C_{TS} by the following equation:

$$C_{H_2S} = C_{TS}\left(\frac{10^{-pH}}{10^{-pH}+10^{-pKa}}\right) \qquad (1)$$

where C_{H2S} and C_{TS} are the concentrations of dissolved hydrogen sulfide and total sulfide, respectively. The acidity constant for hydrogen sulfide, pK_a, is a function of temperature and, based on the Van't Hoff relationship and the standard enthalpy values for H_2S and HS^- (Snoeyink and Jenkins, 1980), can be determined by the following second-order polynomial equation:

$$pK_a = 4.545x10^{-5}*T_L^2 - 1.504x10^{-2}*T_L + 7.447 \quad (2)$$

The solubility of H_2S in water increases at pH values above 7 and as pH shifts from alkaline to acidic ($pH < 7$), the potential for H_2S emissions increases. The sulfide anion can form at $pH > 12$, well above the range for a typical hog lagoon, and so it is not expected to be present in the effluent sampled.

For the physiochemical process of H_2S transfer across the gas-liquid interface, the transfer of the aqueous form ($H_2S_{(aq)}$) into the gaseous form ($H_2S_{(g)}$) can be expressed by:

$$H_2S_{(aq)} \rightarrow H_2S_{(g)} \quad (3)$$

Only the $H_2S_{(aq)}$ fraction, not the ionized form (HS^-), can be transferred across the gas-liquid interface (U.S. EPA, 1974).

Mass Transport Model

The mass transport with chemical reactions model is based on the quiescent thin film concept (Whitman, 1923; Danckwerts, 1970). The principle characteristics of this transport model are depicted in Figure 1.

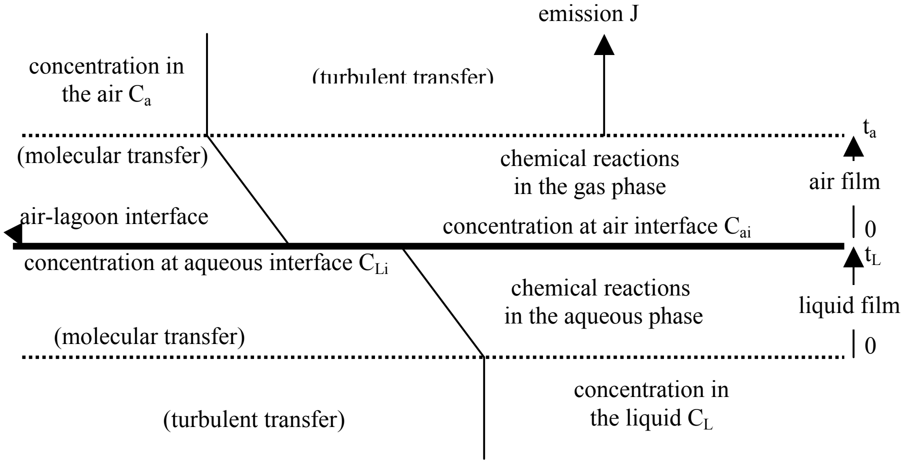


Figure 1. Two film theory of mass transfer

A gas phase film extends upward from the air-liquid interface to the well-mixed air region, and a liquid phase film extends downward from the same interface to the well-mixed liquid region of the lagoon. The film thickness of a given phase was defined as the ratio of the hydrogen sulfide diffusion coefficient for that phase to the mass transfer coefficient as experimentally determined by Mackay and Yeun (1983) for the same phase.

The model explicitly takes into account molecular diffusion and chemical reactions. In the liquid film, only hydrogen sulfide's reversible reaction in water is considered, and pH is assumed constant. Based on these assumptions, a theoretical result of Olander (1960) is used to define the hydrogen sulfide flux, J_i, in the liquid phase at the air-liquid interface:

$$J_i = \left(\frac{D_c}{t_L}\right)\left(C_L - C_{Li}\right)\left(1 + \frac{D_A}{D_c}K_{rL}\right) \quad (4)$$

where A denotes hydrogen sulfide anion [HS^-] and C denotes hydrogen sulfide [H_2S]; D_A and D_c are the diffusivities of hydrogen sulfide anion and hydrogen sulfide, respectively; t_L is the thickness of the liquid film. Hydrogen sulfide concentrations at the interface and in the bulk of the liquid phase are given by C_{Li}

and C_L, respectively. K_{rL} is the overall effective equilibrium constant and is given by $K_{rL} = \frac{K_{H_2S}}{\left[H^+\right]}$ in which K_{H_2S} is the dissociation constant for the equilibrium equation of hydrogen sulfide in the liquid. For the gas phase film, the primary reaction of hydrogen sulfide with the hydroxyl radical [OH] is considered (Seinfeld and Pandis, 1998). In the gas film, [OH] is assumed to have a constant concentration, giving an effective first order reaction for hydrogen sulfide, with first order reaction rate constant in the gas phase, given as

$$k_{ra} = k[\mathrm{OH}] \tag{5}$$

The following equation describes the transport of hydrogen sulfide in the gas phase:

$$D_a\left(\frac{d^2C(z)}{dz^2}\right) = k_{ra} \times C(z) \tag{6}$$

Where C(z) is the hydrogen sulfide concentration at the height of z in a gas film of thickness t_a and D_a is the molecular diffusion of hydrogen sulfide in the gas phase. The boundary conditions are:

$$z = 0;\ C(0) = C_{ai} \tag{7}$$

$$z = t_a;\ C(t_a) = C_a \tag{8}$$

The solution to the mass transport equation results in hydrogen sulfide flux to the atmosphere being expressed in terms of film thickness, gas phase hydrogen sulfide diffusion coefficient, the effective first order rate constant, an the concentrations at the film boundaries.

Assuming the gas phase and liquid phase hydrogen sulfide concentrations at the air-liquid interface are in equilibrium and related by Henry's Law constant (H), Equation 4 can be combined with a gas phase interfacial expression for flux based on the solution to Equation 6. The result is an expression for the flux of hydrogen sulfide from the lagoon water to the atmosphere.

Results

The model reveals that the calculated hydrogen sulfide flux is dependent on several variables, including lagoon temperature, pH, and aqueous hydrogen sulfide content of the lagoon. Lagoon temperature plays a significant role in estimating hydrogen sulfide flux. During model sensitivity analysis, constant values of 7.5, 20.0°C, and 10.0 mg L^{-1} were used for pH, lagoon temperature, and total aqueous sulfide content, respectively. Two values were held constant and one variable altered was in turn to test model performance.

Effects of lagoon temperature include molecular diffusion coefficients in both phases and concentration control through variations of Henry's Law constant and dissociation constant. Measured near-surface lagoon temperature ranged from 9.1 to 32.5°C throughout the year. The model temperature was varied from 2.5 to 40°C.

The chemical equilibrium of the H_2S-HS^- system in aqueous phase is driven by lagoon pH. The pH in the model was varied from 6.5 to 8.5. However, lagoon pH measurements only varied slightly, from 7.8-8.2 and so results from other studies are also used to test the model's sensitivity to this parameter.

The waste from the confinement houses was flushed out with recycled lagoon water and discharged into the lagoon from the top (top-loading). Sulfide is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). During the course of the measurement campaign, the amount of total sulfide in the lagoon ranged from 0.1 to 13.0 mg L^{-1}. The concentration in the model was varied from 0 to 50 mg L^{-1}.

Conclusions

A Coupled Mass Transfer with Chemical Reactions Model was developed in order to accurately predict hydrogen sulfide emission rates from anaerobic waste treatment lagoons. The model reveals that the calculated hydrogen sulfide flux is dependent on several variables, including lagoon temperature, pH, and aqueous hydrogen sulfide content of the lagoon. Model results were compared with field measurements made over the course of a year at a commercial finishing swine farm operating under steady-state conditions.

References

Agency for Toxic Substances and Disease Registry (ATSDR), Center for Disease Control. 2004. Public Health Statement for Hydrogen Sulfide, Draft for Public Comment, CAS # 7783-06-4. http://www.atsdr.cdc.gov/toxprofiles/phs114.html (January 13, 2006).

Aneja, V.P., J.P. Chauhan, J.T. and Walker. 2000. Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *Journal of Geophysical Research* 105 (D9): 11535-11545.

Aneja, V.P., W.H. Schlesinger, D. Niyogi, G. Jennings, W. Gilliam, R.E. Knighton, C.S. Duke, J. Blunden, and S. Krishnan. 2006. Emerging national research needs for agricultural air quality. *Eos Transactions* 87(3): 25-36.

Arogo, J., R.H. Zhang, G.L. Riskowski, and D.L. Day. 1999. Mass transfer coefficient for hydrogen sulfide emission from aqueous solutions and liquid swine manure. *Transactions of the ASAE* 42(5): 1455-1462.

Arogo, J., R.H. Zhang, G.L. Riskowski, and D.L. Day. 2000. Hydrogen sulfide production from stored liquid swine manure: A laboratory study. *Transactions of the ASAE* 43(5): 1241-1245.

Danckwerts, P.V. 1970. Gas-Liquid Reactions, McGraw-Hill Book Company*,* New York.

Lim, T.T., Heber, A.J., Ni, J. Q., Sutton, A.L., and Shao, P. 2003. Odor and gas release from anaerobic treatment lagoons for swine manure. *Journal of Environmental Quality* 32(2): 406-416.

Mackay, D., and T.K. Yeun. 1983. Mass transfer correlations for volatilization of organic solutes from water. *Environmental Science and Technology* 9(13): 211-217.

Olander, D.R. 1960. Simultaneous mass transfer and equilibrium chemical reaction. *AICHE Journal* 6(2): 231-239.

Paerl, H.W. 1997. Coastal eutrification and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. *Limnology and Oceanography* 42: 1154-1165.

Seinfeld, J.H. and S.N. Pandis. 1998. Atmospheric Chemistry and Physics. New York: John Wiley & Sons, Inc. pp.1302-1303.

Snoeyink, V.L., and D. Jenkins. 1980. Water Chemistry. John Wiley and Sons, New York, N.Y: 463 pp.

U.S. Environmental Protection Agency (U.S. EPA). 1974. "Process design manual for sulfide control in sanitary sewerage systems." U.S. EPA Technology Transfer, U.S. EPA, Washington, D.C.

U.S. Environmental Protection Agency (U.S. EPA). 2001. "Emissions from Animal Feeding Operations." EPA Contract No. 68-D6-0011. Emissions Standards Division, Office of Air Quality Planning and Standards, Research Triangle Park, 27711.

Warneck, P. 2000. Chemistry of the Natural Atmosphere*,* Academic Press, San Diego, pp. 589-610.

Whitman, W.G. 1923. The two-film theory of gas absorption. *Chemical and Metallurgical Engineering* 29(4): 146-148.

Zahn, J.A., A.E. Tung, and B.A. Roberts. 2002. Continuous ammonia and hydrogen sulfide emission measurements over a period of four seasons from a central Missouri swine lagoon. ASAE Meeting Paper No. 024080. St. Joseph, MI.

Characterization of Non-Methane Volatile Organic Compounds at Five Confined Animal Feeding Operations in North Carolina

J. Blunden[1], V.P. Aneja[1], and W.A. Lonneman[2]
[1]Box 8208 Jordan Hall, North Carolina State University
Department of Marine, Earth, and Atmospheric Sciences,
Raleigh, NC 27695-8208, U.S.A.
[2]Senior Environmental Employment Program, U.S. Environmental Protection Agency,
Research Triangle Park, NC 27711, U.S.A.

Abstract

Samples were collected and analyzed in a field study to characterize C_2-C_{12} volatile organic compounds (VOCs) emitted at five swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed conventional lagoon and field spray technologies, while three sites utilized various alternative waste treatment technologies in an effort to substantially reduce gaseous compound emissions, odor, and pathogens from these swine facilities. More than 100 compounds, including various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were positively identified and quantified by Gas Chromatographic/Flame Ionization Detection (GC/FID) analysis and confirmed by Gas Chromatographic/Mass Spectrometry (GC/MS). GC/MS analysis of one particularly complex sample collected assisted in providing identification and retention times for 17 sulfur type VOCs including dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide as well as many other VOCs. Highest VOC concentration levels measured at each of the facilities were near the hog barn ventilation fans. Total measured VOCs at the hog barns were typically dominated by oxygenated hydrocarbons (HCs), i.e., ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~37-73% of net total measured VOCs that were emitted from the hog barns at the various sites. Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, were determined to have higher concentration levels at the barns than the background at every farm sampled with the exception of one farm during the warm sampling season.

Introduction

Swine production has increased dramatically over the last decade in North Carolina, making the state the second largest producer of hogs in the United States, with a population of ~10 million animals (NCDA, 2003). In recent years, contract arrangements for production have aided the expansion of hog operations by providing the capital necessary for swine operations to adopt new technologies and achieve major growth (McBride and Key, 2003). More hogs are confined to smaller areas, thereby increasing amounts of odorous and potentially harmful compounds due to a higher amount of excretion.

In response to environmental concern, the North Carolina Attorney General determined that the development of "Environmentally Superior Technologies" (ESTs) would serve well the public interest of North Carolina, with the objective of reducing potentially hazardous emissions from these swine facility sites (Aneja et al., 2003). Project OPEN (Odors, Pathogens, and Emissions of Nitrogen) was established in December 2000 in an effort to evaluate various alternative waste treatment technologies (i.e., ESTs).

Emissions of compounds such as methane and ammonia from swine facilities have been well documented (McColloch et al., 1998; Sharpe and Harper, 1999; Walker et al., 2000; Aneja et al., 2001; Childers et al., 2001). This study focuses exclusively on the characterization of C_2-C_{12} volatile organic compounds (VOCs) present in the ambient air at various swine facilities located in the eastern region of North Carolina and may be regarded as a survey to determine various gaseous compounds. Some of these compounds are associated with unpleasant odors in this type of rural environment. VOC sample collection strategy was designed to assess VOCs from suspected emission sources at the various potential ESTs and conventional swine farm locations. Samples were collected at the housing areas as well as the technologies (i.e., storage lagoons) at all sites.

VOCs have been reported from several swine farms in Eastern North Carolina to investigate odor complaints (Schiffman et al., 2001a). The compounds detected in this study include various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides. Sulfides and phenols have long been associated with odor problems at swine facilities (Hammond et al., 1989; O'Neill and Phillips, 1992). Results presented consist of the high C_2-C_{12} VOCs levels observed from the ventilation fans at the hog confinement barns. Concurrently collected samples of background air are included to more clearly determine the VOCs resulting from hog barn activities.

Methods

Experimental Research Site Descriptions

Samples were collected at four different farms and one laboratory site located in Eastern North Carolina. Three sites utilized various ESTs to treat animal waste while two sites maintained a conventional waste treatment technology. Each farm was sampled during one warm and one cool season. Each site and related waste treatment technology is briefly described below:

Barham Farm is a 4,000 head farrow to wean operation located near Zebulon, North Carolina (35.70°N, 78.32°W, 130m MSL). Each hog barn contained a fan ventilation system, sometimes referred to as tunnel ventilated. This site utilized a covered in-ground ambient digester as a potential alternative waste treatment system. The in-ground ambient digester may be considered as a primary treatment lagoon (4,459 m^2) that had an impermeable polypropylene covering over its surface. All the emitted gases including methane and other organic gases were collected under the cover and periodically extracted and delivered to a generator system where the gases were converted to electricity. The effluents from the hog barns were initially directed to the primary lagoon with the impermeable cover and the effluent then flowed through a single outlet pipe into a secondary storage lagoon (19,398 m^2). Here, the liquid waste was treated via a de-nitrification/biofiltration process. The treated wastewater was then used for two purposes: to flush fresh effluent from the hog barns and as a spray over agricultural crops for nutrient enrichment purposes (Cheng et al., 2000).

Grinnells Laboratories is located on the North Carolina State University campus in Raleigh, NC (35.47°N, 78.40°W, 107 m MSL). It should be taken into account that this site was located in a non-rural area. This site utilized a Ganet-Fleming Belt System that consisted of the retrofit installation of a conveyor belt type apparatus in the swine production facility to convey the manure wastes generated therein. The process separated the liquid wastes and the solid wastes as they were deposited inside the production facility. The solids were then managed through a gasification process, which involves the burning of a substance in a low-oxygen environment to convert complex organic compounds to gases. The gases were collected and used to make fuel-grade ethanol. The liquids received further treatment via a sequencing batch reactor. There is no storage lagoon located at this site (Koger et al., 2000).

Howard Farm, located near Richlands, NC (34.84°N, 77.50°W, 5 m MSL), utilized a "Solids separation/Constructed Wetlands" system as its potential waste treatment system. Effluents from the hog barns were directed initially to a solid separator where the solid waste was separated from the liquid waste. The solids were then removed to an off-site facility and liquid waste was put into two outer lagoon cells (outer cell 19,366 m^2; inner cell 10,256.3 m^2). As the wastewater traveled around the cells, it encountered the constructed wetlands, which treated the wastewater effluent through microbial utilization and the root substrate of the wetland plant species. The treated wastewater was then filtered into a finishing lagoon (7,428 m^2) where it was used in a manner similar to Barham Farm, i.e., the wastewater was recycled to flush more effluent through the hog barns and as a spray for agricultural crops. Containment houses located on the property utilized a fan ventilation system (Humenic, 2000).

Stokes Farm and Moore Brothers Farm operate a conventional (i.e., lagoon and spray) technology as the primary means of handling effluent. This method of waste treatment is the same type that is currently used by most farms in North Carolina. Effluents flow from the hog barns into an on-site storage lagoon. This wastewater is then used to flush effluent from the houses and as spray over agricultural crops. Stokes Farm is located near Greenville, NC (35.43°N, 77.48°W, 17 m MSL). The storage lagoon is 15,170 m^2 and the hog barns utilize a natural ventilation system. Moore Brothers Farm is located in Jones County near

Kinston, NC (35.14°N, 77.47°W, 13 m MSL). The storage lagoon is 30,630 m^2 and the confinement houses on site employ fan ventilation.

Sample Collection and Sampling Strategies

Ambient air samples were collected in 6-Liter electropolished stainless steel SUMMA canisters, evacuated to a sub-ambient pressure of <0.05 mm Hg. During sample collection, the valve on the canister was opened slowly over a timeframe of ~4 minutes and then fully opened on the order of 1 minute, thus allowing for a ~5 minute point sample to be collected.

Samples were collected during the 12:00-13:00 Eastern Standard Time (EST) period at various suspected source areas including lagoons, barn ventilation fans, and at "strong" odorous areas, determined through sense of smell, for each particular site. Simultaneous samples were collected at upwind and downwind locations on the farms in an effort to determine VOCs originating from the farm.

VOC Sample Analysis

The canister samples were taken to the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (EPA) located in the Research Triangle Park, NC, where they were analyzed using gas chromatographic (GC) procedures. All samples were analyzed by GC flame ionization detection (FID) combined with a cryogenic preconcentration approach. The GC column was a 60m x 0.32mm ID fused silica column with a 1μm liquid phase thickness (J & W Scientific, Folsom, CA). The GC column was temperature programmed and consisted of a -50°C initial temperature for two minutes followed by temperature programming to 200°C at a rate of 8°C/minute. After a 7.75 minute hold period, the column temperature is programmed to 225°C at 25°C/minute rate and held at that temperature for 8 minutes. This temperature programming sequence provided separation of the C_2-C_{12} compounds and conditioned the column for proceeding samples. Liquid nitrogen is used as the cryogen to obtain sub-ambient temperatures.

The GC/FID system was calibrated using 0.25 ppm propane in air NIST SRM (National Institute of Standards and Technology Standard Reference Material). Compound identification was determined using a CALTABLE consisting of more than 300 VOCs with corresponding column retention times.

A gas chromatograph equipped with a mass spectra detection system (GC/MS) (Hewlett-Packard Model 6890/5972, Avondale, CA) was used to verify compound peak identification. The GC/MS system served to both verify compound identification as well as to identify unknown compound peaks. Generally, 1-2 samples collected during each sampling campaign were selected for GC/MS analysis, based on the observed high peak concentration levels and/or the occurrence of unknown peaks.

Results

Measurement campaigns for this study were conducted as the farms became steady-state with the individual technologies in place. Due to the nature of Project OPEN, the farms were available for sampling for about two week increments in each warm and cold season, resulting in some limitations of our sampling strategies. The data results presented here consist of one day sampling at each swine farm facility for both warm and cold seasons. Highest VOC concentrations were typically observed at the hog barn ventilation locations for all sites. These specific results provide the most suitable database to compare both composition and concentration differences between sites and for both seasons.

Identification of the VOCs with the GC Systems

Using a GC/FID approach, individual VOCs are identified by column retention time using a detailed CALTABLE containing known VOCs and their corresponding retention times prepared from the analysis of known VOC mixtures. At the outset of this study, the GC column retention times for many of the sulfur containing VOCs were unknown. A sample collected at the outlet of a pipe leading from the covered lagoon to the electric generator system at the Barham Farm during the April sampling period greatly assisted in the identification of many of these sulfur compounds. This pipe transported methane as well as other organic gases produced from a primary treatment lagoon fitted with an impermeable cover to a generator system that converted these gases to electricity. The GC/FID analysis results of this sample indicated a complex pattern of peaks, several of which were not in the existing CALTABLE. The sample served to demonstrate the complex VOC mixture produced by the treatment of hog waste that may be released to the ambient air. The processed sample using the established CALTABLE for GC peak identification indicated the presence of several unidentified peaks. Analysis of this canister by GC/MS provided identification to many of the unidentified compounds observed with the GC/FID analysis. Since identical GC columns and temperature programming approaches were used for both GC systems, the unidentified peaks observed on the GC/FID system were located on the GC/MS system and compound identifications were determined.

Sulfides were of particular interest because many produce distinct malodors. Seventeen sulfur-type VOCs were identified, including thiophene, 2-methylthiophene, 3-methylthiophene, methyethyldisulfide, 2-ethylthiophene, 2,5-dimethylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, methylisopropyldisulfide, methylpropyldisulfide, methyl-sec-butyldisulfide, and dimethyl tetrasulfide and eventually added to the GC/FID CALTABLE to use for the other canister samples collected at the swine farm sites. The three largest peaks observed from the GC/FID at column retention times later than isobutane were dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide. These compounds represented 21.1, 17.7, and 24.4%, respectively, of the total concentration of all the GC compound peaks eluting from the column between isobutane and the last observed GC compound peak. No neat compounds or standard mixtures were available for 100% positive identification of these compounds; however, compound molecular weight and boiling point were considered to be appropriate for observed GC column retention times. Two other sulfur-containing VOCs also observed in the GC/MS results included carbonyl sulfideand carbon disulfide. Neither compound is expected to respond in the FID and would therefore not be determined with the GC/FID results. Other VOCs identified in the sample by GC/MS included alkanes, alkenes, ketones, and aldehydes.

To evaluate storage stability, this complex sample first analyzed on May 13, 2002 was stored in the laboratory for more than a seven-month period and reanalyzed by both GC/FID and GC/MS on two separate occasions: July 11, 2002, and January 31, 2003. The sulfur-type VOCs are considered to be unstable in SUMMA canisters and quickly removed by the container surfaces. With some exceptions, the composition of the compounds remained stable upon reanalysis. Particularly, several of the sulfur-type VOCs were observed to be quite stable. Almost no change was observed for dimethyl sulfide over the 7 month period. Two other sulfur-type VOCs, i.e. dimethyl disulfide and dimethyl trisulfide, appear to undergo conversion rather than surface loss. Over the 7 month storage period the 17.7 to 32% increase in dimethyl disulfide appears to be compensated by the 24.3 to 7.3% loss of dimethyl trisulfide. Loss, or most likely conversion, of the lesser abundant dimethyl tetrasulfide also occurs during the 7 month period. The reason for the dramatic change in these compounds is unclear. The hydrocarbon-type VOCs appear to be quite stable over the storage period. Canister surface passification by water vapor in the canister is credited for storage stability.

VOCs Observed at Hog Barns

Highest VOC concentrations generally observed at each of the five swine facilities were sampled at the barn ventilation locations. With the exception of Stokes, this location was directly in front of the fan ventilation systems. At the Stokes site, natural open-air barn ventilations are utilized rather than ventilation fans and samples collected next to or between the barns were selected for comparison. To better evaluate the VOCs coming from the barns, corresponding background (i.e., upwind) samples were simultaneously collected when the barn ventilation fans were sampled.

It is expected that the observed VOC composition at the ventilation outputs consists of background ambient air combined with VOC sources within the barn facility. Ideally, activities within the hog barns at each of the different site locations are expected to be uniform; however, it should be noted that the number of animals as well as the animal weights, size, and type (i.e., farrowing or finish) vary from barn to barn as well as farm to farm and could affect observed VOCs measured.

Figure 1 depicts the percent contribution of the various characteristic types of identified VOCs observed at the hog barns. Percentage values were determined by summing the individual VOCs into the various compound types and ratioing these groups to total identified VOC. Oxygenated VOCs appear to be the most abundant compounds observed near the barns. Similarities are observed in terms of specie composition near the various barns at the different sites; however, concentration levels tended to vary quite a bit, although all were within the same order of magnitude. Acetaldehyde, methanol, ethanol, and acetone were among the most dominant compounds measured near the barns. These four compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at EST facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Many of these samples were analyzed by GC/MS to confirm compound identification.

Net acetaldehyde concentration, at Barham, during both sampling periods in April and November, were 16.23 ppbC and 40.12 ppbC, respectively. At Grinnells in November the net acetaldehyde concentration was determined to be 9.57 ppbC; however, acetaldehyde was not observed at a higher concentration level at the ventilation exhaust than the background sample in April. At the EST sites, ethanol was a dominant compound among all measured VOCs at all farms with the exception of Grinnells in April. Ethanol net concentration levels at Barham were 47.09 and 155.41 ppbC representing 16.6 and 40.1% of net total measured VOCs originating in the barn), in April and November, respectively. At Grinnells, ethanol net concentration was 110.74 ppbC in November (31.5% of net total measured VOCs), and 43.95 and 82.75 ppbC net concentrations at Howard in June and December, (58.8% and 38.5% of net total measured VOCs), respectively. Ethanol concentrations at the two farms utilizing conventional waste treatment methods were comparable, e.g., at Stokes in September (67.65 ppbC net concentration and 28.7% of net total measured VOCs), and at Moore in February (18.7 ppbC net concentration and 22.8% of net total measured VOCs). Ethanol was not observed as a dominant compound at Moore in October. Considering the seasonal variability of these observations, temperature does not appear to be the primary or only determining factor in the concentration levels in these sample locations. High levels of methanol concentrations were observed at several sites. At Barham, during both April and November sampling episodes, the observed methanol concentration of 42.9 ppbC and 26.1 ppbC represented 15.1 and 6.8%, respectively, of net total measured VOCs originating in the barn. At Grinnells in April, methanol concentrations were measured at 23.3 ppbC (20.2% of net total measured VOCs originating in the barn). Acetone was a dominant compound in the hog barns at all farms with the exceptions of the EST sites, Howard and Barham in June and November, respectively. At all sites where comparisons were made, acetone contributed ~3-12% of the net difference for total measured VOCs.

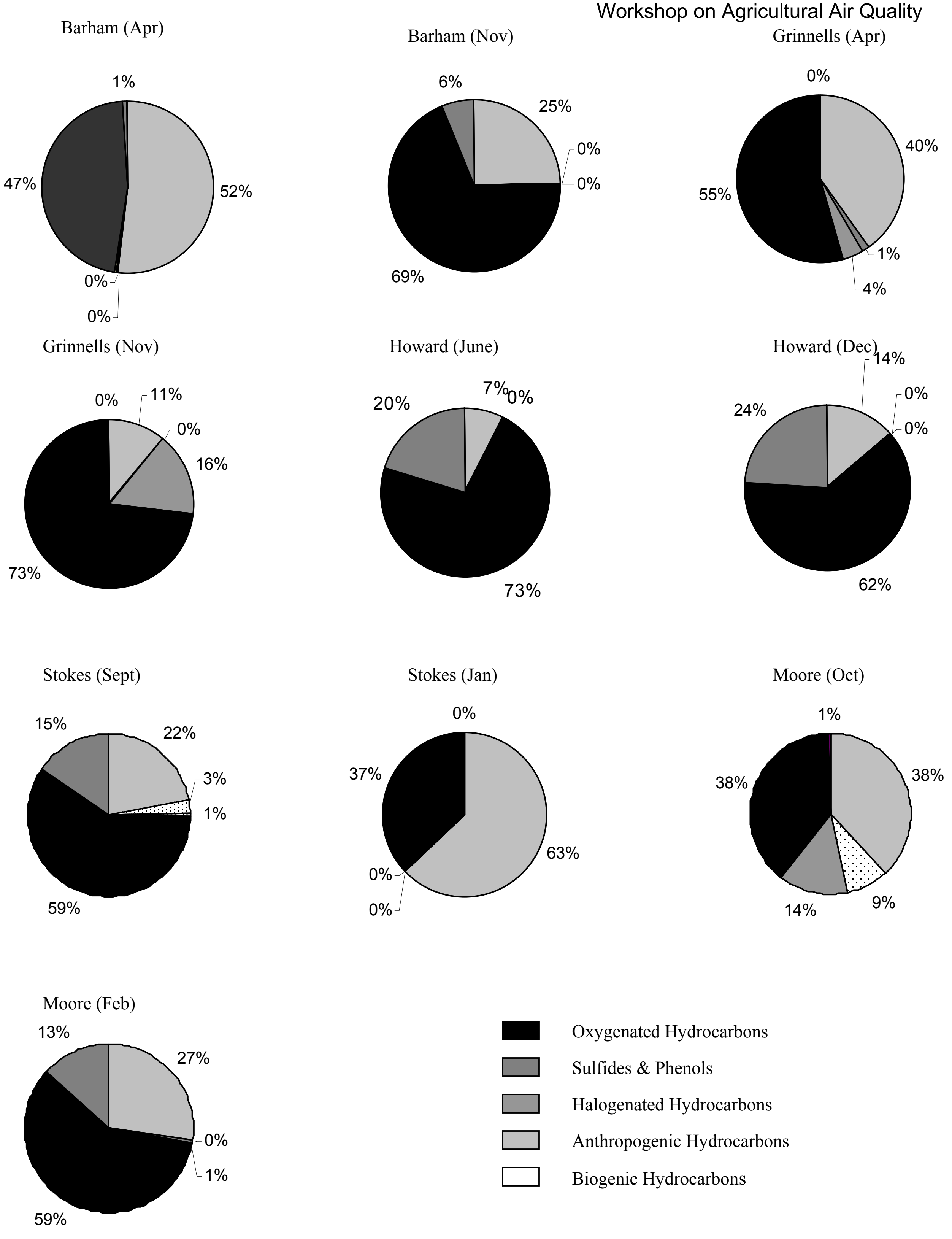


Figure 1. Total percent contributions of various types of dominant VOCs observed within ~1 meter of hog barn ventilation systems at each of the sampling sites. Sampling for each site was conducted during one warm and one cold season

Detected Sulfur and Phenolic Compounds

Dimethyl sulfide and dimethyl disulfide were the two sulfur-type VOCs frequently observed at all of the site locations that were verified by GC/MS and quantified by GC/FID. These compounds are recognized as malodorous VOCs with odor thresholds, defined as the concentration at which odor is first detected, of 2.24 and 12.3 ppb, respectively (Schiffman et al., 2001a). Dimethyl sulfide was measured at levels above its odor threshold at Barham in November, (14.4 ppbC net total concentration) and at Howard in December (6.6 ppbC net total concentration). At the barn ventilation systems for all sites, dimethyl sulfide was measured above the respective background levels with the exception of Stokes Farm in January. In this instance, the levels were comparable, 0.21 ppbC measured at the barns and 0.25 ppbC upwind. For all sites, dimethyl sulfide was detected in the background ambient air with the exceptions of Grinnells in April. At the barn ventilation systems, dimethyl disulfide was detected at the EST sites Barham, Grinnells, and Howard, during both sampling episodes. For the conventional sites, dimethyl disulfide was detected at Moore during both sampling episodes and at Stokes in September. Highest concentration levels were measured at Howard Farm, 0.77 ppbC and 2.15 ppbC, in June and December, respectively. Dimethyl disulfide was not measured (i.e., below detectable limits) in the upwind samples during any of the sampling episodes at the conventional sites. Dimethyl disulfide was measured at ≤ 0.12 ppbC at Barham in April, Grinnells in November, and Howard in June, and was below detectable limits for the other sampling episodes at the EST sites. Observed concentration levels for dimethyl disulfide at all sites never approached the 12.3 ppb odor threshold level. Figure 2 provides a comparison of the concentrations of these reduced organic sulfur compounds emitted from houses with their average concentrations in the ambient air around swine facilities. Another malodorous compound associated with swine farms, 4-methylphenol, which has an odor threshold of 5.3 ppb (Van Gemert and Nettenbreijer , 1978), was measured at the barns at the EST sites, Barham, Grinnells, and Howard during each sampling campaign. Highest concentrations of 4-methylphenol were measured at Howard in June and December, 12.5 ppbC net concentration (16.7% of net total VOCs) and 43.3 ppbC net concentration (20.1% of net total VOCs), respectively, at Stokes in September (32.7 ppbC net concentration, 13.9% of net total VOCs) and at Moore in February (10.50 ppbC and 12.8% of net total VOCs). 4-methylphenol was not detected at Stokes at all during the January sampling period or at Moore in October. To convert the measured ppbC concentrations of 4-methylphenol to ppb, an ECN value of 6.38 was used (Jorgenson et al., 1990). Only the December measurement at Howard, i.e., 43.3 ppbC/6.38 or 6.78 ppb, exceeded the compound odor threshold of 5.3 ppb.

We note that carbonyl sulfide and carbon disulfide were detected through GC/MS analyses but could not be determined by the GC/FID. Known standards of these compounds were not available to obtain quantitative results with the GC/MS system. Carbon disulfide has an odor threshold of ~16 ppb and there is no known odor threshold established for carbonyl sulfide (USDHHS, 1993). Schiffman *et al*. (2001b) determined that intensity of the odorous emissions from swine facilities resulted from the combined effect of odorous compounds present at sub-threshold concentrations in addition to individual compounds observed above their respective odor threshold levels.

The reduced organic sulfur compounds observed at the exhaust ventilation fans of each farm were normalized by live animal weight (LAW) in the barn (ppbC/1000kg). These results are presented in Figure 3. It is important to keep in mind that the age and type of animal, in addition to LAW, varied from farm to farm. At Barham, concentration levels were 0.021 ppbC/1000kg and 0.046 ppbC/1000kg in April and November, respectively. At Grinnells total levels were 0.079 ppbC/1000kg in April and 0.411 ppbC/1000kg in November. At Howard sulfur concentrations were 0.068 ppbC/1000kg in June and 0.141 ppbC/1000kg in December. Grinnells had the overall highest normalized concentration during the November sampling period. The lowest normalized levels of dimethyl sulfide and dimethyl disulfide were observed at Moore where concentrations were 0.007 ppbC/1000kg in both October and February. Normalized concentration levels for these sulfur-type VOCs were consistently higher during the colder season than the warmer season at each of the farms (Figure 3) with the exception of Moore, where the normalized concentration levels were the same.

Many of the other sulfur-type VOCs were observed to have very small percent concentrations. These compounds may be present but concentration levels are below detectable limits. It is unlikely that the percent compositions of the detected compounds remained the same after emission into the ambient air.

This is due to dispersion, vertical mixing, and/or photochemical reactions that occur in the atmosphere near ground level.

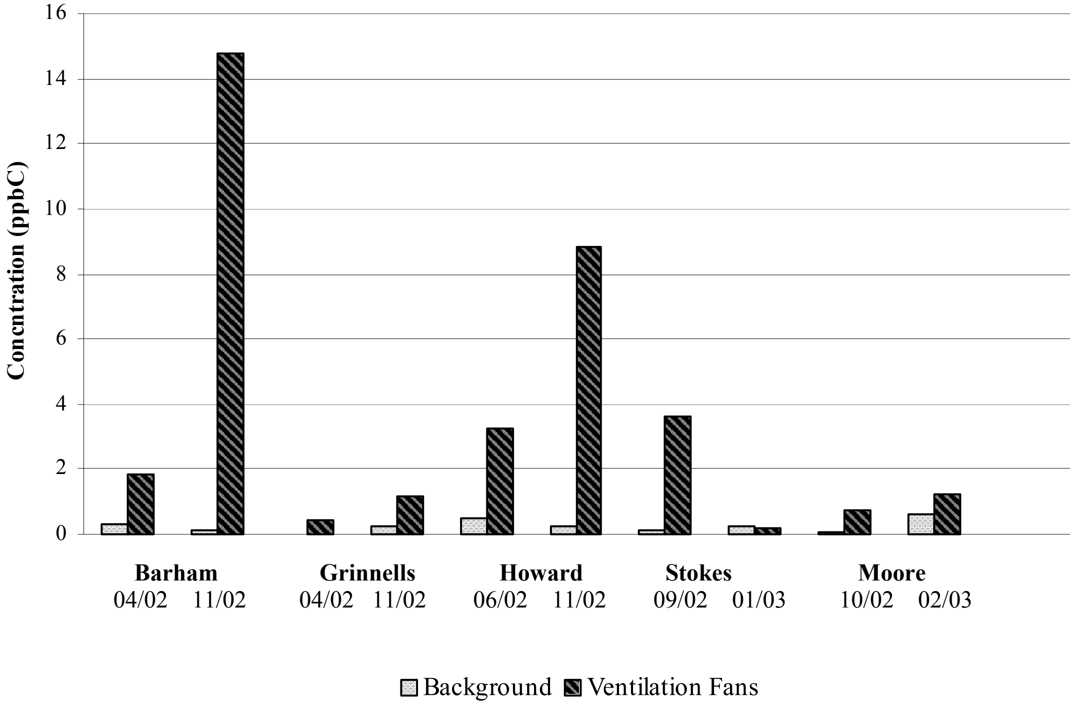


Figure 2: Total reduced organic sulfur (dimethyl sulfide and dimethyl disulfide) concentrations (ppbC) at various swine facilities in Eastern North Carolina

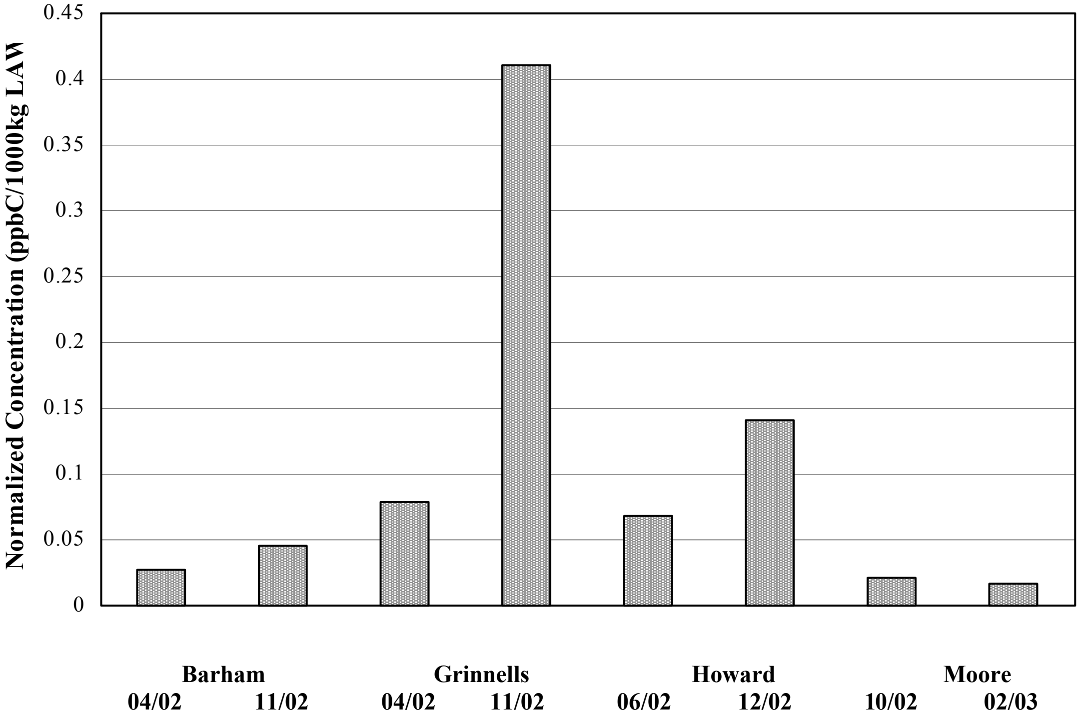


Figure 3: Total reduced organic sulfur concentrations (dimethyl sulfide and dimethyl disulfide) (ppbC) detected at ventilation fans, normalized by live animal weight (LAW)

Conclusions

A total of 110 samples were collected by means of SUMMA electropolished stainless steel canisters to characterize volatile organic compounds (VOCs) detected at five swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed traditional lagoon and field spray technologies; while three sites utilized various potential ESTs in an effort to reduce ammonia and VOCs emissions, odor and odorants, and pathogens at swine farms. More than 100 compounds, including various paraffins, aromatics, olefins, ethers, monoterpenes, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were identified and quantified by GC/FID analysis. Many of these compounds have been determined to play an important role as precursors to tropospheric ozone, fine particulate matter (PM_{fine}), and other atmospheric photochemical oxidation formation such as peroxyacetal nitrate (PAN) (Kang et al., 2001). Other compounds observed (e.g., reduced organic sulfur compounds) are related to odor and irritation senses (Schiffman et al., 2001b; Kuroda et al., 1996).

One complex sample collected at Barham Farm helped to characterize several sulfur-type VOCs, including dimethyl sulfide and dimethyl disulfide. Carbonyl sulfide and carbon disulfide were positively identified by GC/MS analysis but could not be quantitatively determined by GC/FID. Another compound commonly associated with malodors at swine facilities as well as general air toxicity, 4-methylphenol, was also identified in many of the GC/FID sample results and verified by GC/MS analysis. The GC/MS analysis of selected samples also served to verify and/or identify many VOCs reported here.

Overall, the highest VOC concentration levels measured at each of the sites were in close proximity to the hog barns. The dominant compounds observed near the hog barns from each sampling period were compared with background samples (i.e., upwind of lagoons and houses) collected in the same timeframe, with the difference referred to as the net concentration. The total measured VOCs at the hog barns were typically dominated by ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at EST facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Several of these compounds, most particularly acetaldehyde, may participate in the photooxidant process to produce downwind photochemical ozone.

Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, had concentration levels at the barns above the background concentration at every farm sampled with the only exception of Stokes in September. Dimethyl sulfide was measured at levels above its odor threshold (2.24 ppb) at Barham in November (7.2 ppbC net total concentration) and Howard in Decmeber (3.3 ppbC net total concentration). Grinnells had the overall highest normalized concentration of dimethyl sulfide and dimethyl disulfide during the November sampling period (0.411 ppbC/1000kg) while the lowest normalized levels were observed at Moore where concentrations were 0.007 ppbC/1000kg in both October and February. Normalized concentration levels for these sulfur-type VOCs were consistently higher during the colder season than the warmer season at each of the farms with the exception of Moore, where the normalized concentration levels were the same. 4-methylphenol, another odorous compound associated with swine waste was also measured at higher levels near the barns than the background levels at Barham and Grinnells in April, Howard and Stokes during each sampling campaign and at Moore in February. The largest net concentrations of 4-methylphenol were measured at Howard Farm in June and December, at 12.47 ppbC and 43.41 ppbC (16.7 and 20.2% of net total measured VOCs), respectively, and at Stokes Farm in September (32.7 ppbC net concentration, 13.9% of net total measured VOCs).

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References

Aneja, V.P., B. Bunton, J.T. Walker and B.P Malik. 2001. Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons. *Atmospheric Environment* 35: 1949-1958.

Aneja, V.P., S. Schiffman, M. Sobsey, D.S. Kim, S.P. Arya, D.Dickey, L.Stefanski, H.T. Nagle, W. Robarge, P. Westerman, M. Williams, O.D. Simmons, L.Todd, R.L. Seila, R. Mathur, R. Gannon, H. Kimball, and P. Roelle. 2003. Development of Environmentally Superior Technologies: Year Three Progress Report for Technology Determination per Agreements between the Attorney General of North Carolina, Smithfield Foods, Premium Standard Farms and Frontline Farmers. Animal and Poultry Waste Management Center, North Carolina State University, Raleigh, N.C..

Cheng, J., D.H. Willets, and M.M. Pett. 2000. Development of Environmentally Superior Technologies per Agreements between the Attorney General of North Carolina, Smithfield Foods, Premium Standard Farms and Frontline Farmers: Ambient Temperature Anaerocic Digester and Greenhouse for Swine Waste Treatment and Bioresource Recovery at Barham Farm. Animal and Poultry Waste Management Center, North Carolina State University, Raleigh, N.C.

Childers, J. W., E. L.Thompson Jr., D.B. Harris, D.A. Kirchgessner, M. Clayton, D.F. Natschke, and W.J. Phillips. 2001. Multi-pollutant Concentration Measurements Around a Concentrated Swine Production Facility Using Open-Path FTIR Spectrometry. *Atmospheric Environment* 35: 1923-1936.

Hammond, E. G., C. Heppner, and R. Smith. 1989. Odors of Swine Waste Lagoons. *Agriculture, Ecosystems, and Environment* 25: 103-110.

Humenic, F.J. 2000. Development of Environmentally Superior Technologies per Agreements between the Attorney General of North Carolina, Smithfield Foods, Premium Standard Farms and Frontline Farmers: Solids Separation/Constructed Wetlands. Animal and Poultry Waste Management Center, North Carolina State University, Raleigh, N.C.

Jorgenson, A.D., K.C., Picel, and V.C. Stamoudis. 1990. Prediction of gas chromatography flame ionization response factors from molecular structure. *Analytical Chemistry* 62: 683-689.

Kang, D., V.P. Aneja, R.G. Zika, C. Farmer, and J.D. Ray. 2001. Nonmethane hydrocarbons in the rural southeast United States National Parks. *Journal of Geophysical Research* 106: 3133-3155.

Koger, J.B, T. van Kempen, and G.A. Wossink. 2000. Development of Environmentally Superior Technologies per Agreements between the Attorney General of North Carolina, Smithfield Foods, Premium Standard Farms and Frontline Farmers: Belt Manure Removal and Gasification System to Convert Dry Manure Thermally to a Combustible Gas Stream for Liquid Fuel Recovery. Animal and Poultry Waste Management Center, North Carolina State University, Raleigh, N.C.

Kuroda, K., T. Osada, M. Yonaga, A. Kanematu, T. Nitta, S. Mouri, and T. Kojima. 1996. Emissions of malodorous compounds and greenhouse gases from composting swine feces. *Bioresources Technology* 56: 265-271.

McBride, W.D. and N. Key. 2003. Economics and Structural Relationships in U.S. Hog Production.AER-818, U.S. Department of Agriculture, Economic Research Service, Washington, DC.

McCulloch, R. B., G. S. Few, G. C. Murray. and V.P. Aneja. 1998. Analysis of ammonia, ammonium aerosols and acid gases in the atmosphere at a commercial hog farm in eastern North Carolina, USA. *Environmental Pollution* 102 (1): 263-268.

NCDA Agricultural Statistics Division, North Carolina Department of Agriculture and Consumer Services, P.O. Box 27767, Raleigh, NC, 27611, 2003.

O'Neill, D.H. and V.R. Phillips. 1992. A review of the control of odour nuisance from livestock buildings: Part 3, Properties of the odorous substances which have been identified in livestock wastes or in the air around them. *Journal of Agricultural Engineering Research* 53: 23-50.

Schiffman, S.S., J.L. Bennett, and J.H. Raymer. 2001a. Quantification of odors and odorants from swine operations in North Carolina. *Agricultural and Forest Meteorology* 108: 213-240.

Schiffman, S.S., B.W. Auverman, and R.W. Bottcher. 2001b. Health effects of aerial emissions from animal production waste management systems. In: Proceeding of international symposium:Addressing animal production and environmental issues. Raleigh, North Carolina State University.

Sharpe, R.R. and L.A. Harper. 1999. Methane emissions from an anaerobic swine lagoon, *Atmospheric Environment* 33: 3627-3633.

U.S. Departmeny of Health and Human Services (USDHHS). 1993. Hazardous substances Data Bank. National Toxicology Information Program, National Library of Medicine, Bethesda, MD.

Van Gemert, L.J. and A.H. Nettenbreijer. 1978. Compilation of odour threshold values in air and water. *Water Research* 12: 503.

Walker, J.T., V. P. Aneja and D.A. Dickey. 2000. Atmospheric transport and wet deposition of ammonium in North Carolina, *Atmospheric Environment* 34: 3407-3418.

Changes of Climate, Air Pollution and Growing Season in Correlation with Changes of Sun Activities

Horst Borchert
Johannes-Gutenberg University Mainz, Geographic Institute
Westring 159, D-55120 Mainz, Germany, BCHT01@aol.com

Abstract

Continuous Measurements of air pollution and meteorological components in Europe within the last 30 years show strong changes between 1987 and 1991. After this event, we call it "Climate Jump II", SO2-based winter smog-alert-systems were cancelled and Ozone-based summer smog-alert-systems were introduced. These changes were caused by a sudden increase of temperature combined with an increase of global radiation. Both were caused by reduction of clouds initiated by a reduction of cosmic rays (neutrons) within the 22nd sunspot period: Sun observations of NASA show a stronger increase of eruptions of protons producing stronger solar winds, which were reducing cosmic radiation by magnetic deflections during this and the following period. The Climate Jump with increasing ground near temperature of about 1.2 °C in Central Europe seems to be sun made. Moreover the North Atlantic Oscillation (NAO) shows correlation with neutron flux. This leads to the assumption, that there is a causal connection between sunspot controlled cosmic rays and cloudiness, which finally leads during increasing sun activities to increasing temperature and prolongation of growing seasons in Central Europe.

Keywords: Air pollution, Climate change, Global temperature, Global radiation, Cloudiness, Cosmic radiation, Sunspots, Neutron flux, 22nd Sunspot period, North Atlantic Oscillaton, Growing Season,

Introduction

The widely forested German country Rhineland-Palatine with its industrialised towns Mainz and Ludwigshafen seems to be an area representative for Central Europe. The components SO2, Particular Matter (PMx), O3 and NO2 and meteorological components there are measured by the telemetrical controlled system ZIMEN with 31 measuring stations in forested regions and towns (ZIMEN, 2005). By Comparing trends in air pollutants and meteorological parameters one can see remarkable coincidental changes of all components between 1987 and 1991: The concentrations of SO2 and Particle Matter (PMx) decreased by more than 30 %, while Ozone concentrations, temperature and global radiation increased significant within this short time interval of only 4 years (Fig.1). As a consequence winter smog-alert systems (introduced in 1985 and concerning SO2, PMx, NO2 and CO) were cancelled and summertime smog-alert systems concerning O3 were introduced. The strong decrease of SO2 and PMx was seen mainly as a result of successful legal management to reduce emission. The strong increase of anthropogenic O3-concentrations was seen as a result of the increase in traffic (Borchert, H., 1998).

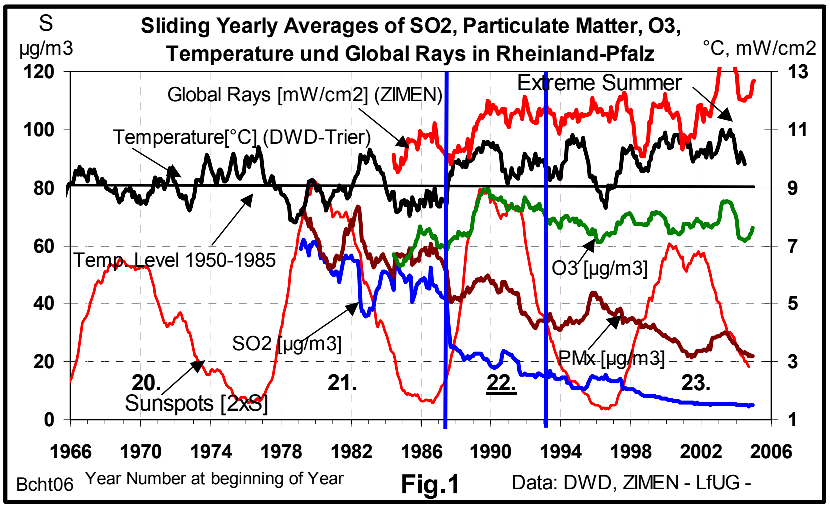
But these strong changes of pollutants since 1987 were accompanied by very strong increase of air temperature and of intensity and duration of sunshine, caused by reduction of cloud cover. It was supposed that these sudden changes of anthropogenic air pollution in this short time interval came from meteorological changes, which were combined with climate change in Europe caused by extraterrestrial influences (Borchert H., 2004).

In the following there are shown the causes of this opinion and further data to prove and stable this opinion.

Change of Temperature and Air Pollutants

The simplest method to describe climate is to study temperature.

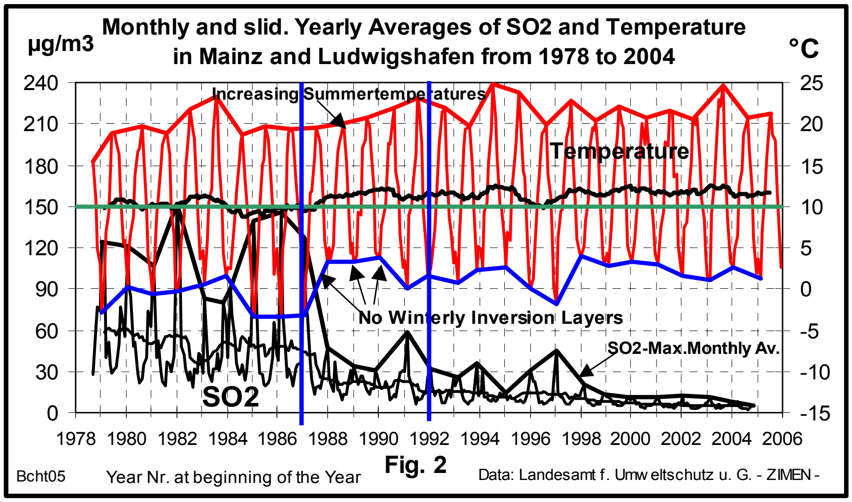
During wintertime the monthly averages of temperature before 1987 were relatively cold (lower than 0°C, Fig. 2). The concentrations of SO2 were high. The main part of SO2 came during this time from power plants of the eastern COMECON countries, transported by cold and dry north eastern winds beneath inversion layers of about 800 m height. In wintertime 1988/89 these cold eastern winds vanished and the measured concentrations of SO2 and dust in western Germany decreased very strong, while the emissions in the eastern countries remained unchanged. Only after 1991 emissions also stopped by collapse of the emitting industries in the eastern countries and by legal reductions of emissions of power plants.



Sliding Yearly Averages of SO2, Particulate Matter, O3, Temperature und Global Rays in Rheinland-Pfalz

Fig.1

Data: DWD, ZIMEN - LfUG -



Monthly and slid. Yearly Averages of SO2 and Temperature in Mainz and Ludwigshafen from 1978 to 2004

Fig. 2

Data: Landesamt f. Umweltschutz u. G. - ZIMEN -

Since 1989 the coldest monthly averages of temperature in wintertime are about 2 °C higher than before.

The Trend of the warmest summer temperatures increased from 1988 to 1991 by about 3 °C. After this jump of the temperature the trend of the warmest monthly temperatures was almost until now.

The trend of the sliding yearly averages of the temperature increased between 1988 and 1991 about 1.2 degrees Celsius and remains in this higher value until now.

Sliding yearly averages of NO2 in the industrialised towns Mainz and Ludwigshafen show the typical development of mainly traffic-induced immissions in western Germany (Fig3). NO2 increased in the early eighties very strongly and reached in 1984 nearly the legal limit value of 80 µg/m3 (annual mean) in these towns. With the introduction of more efficient motors and legal emission control of vehicles and of industry the immissions of NO2 decreased since 1984

But with increasing temperature since 1988 NO2 goes up again and we observe a new maximum in 1990 during this warm period. After this since about 1992 NO2 shows a continuous reduction, caused mainly by the introduction of the catalyst.

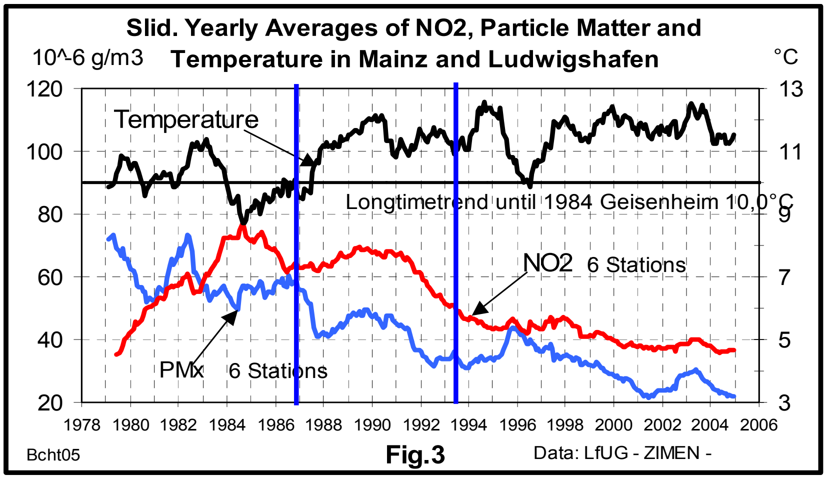


Fig.3

PMx - concentrations showed a similar behaviour to SO2 until 1988. From 1987 to 1988 PMx decreased as a result of the above-mentioned disappearance of pollution transports from eastern regions. From 1988 to 1990 PMx increased again, but now parallel with NO2. This phenomenon points to traffic as a common source of both components. Up to 1988 PMx was mainly caused by industry and power plants, after this till now it seems to be more caused by traffic. The actual PMx-level is less than a third of the level of 1987. Now it is regarded as more dangerous for human health than former knowledge believed – especially its finer parts. The new legal PM10-limits of the European Union are sometimes exceeded in towns.

Jump of Temperature in Central Europe

As ZIMEN started in 1978, we had to look for longer time measurements of meteorological components to study transport phenomena of air pollution over the landscape. To find alternations in relation to earlier times, we studied the data measured by the Deutsche Wetterdienst (www.dwd.de) at about 40 measuring points all over Germany, partly since 1900. The sliding yearly averages of the published temperatures of the DWD do not show any significant increase of long time trend between about 1940 and 1986.

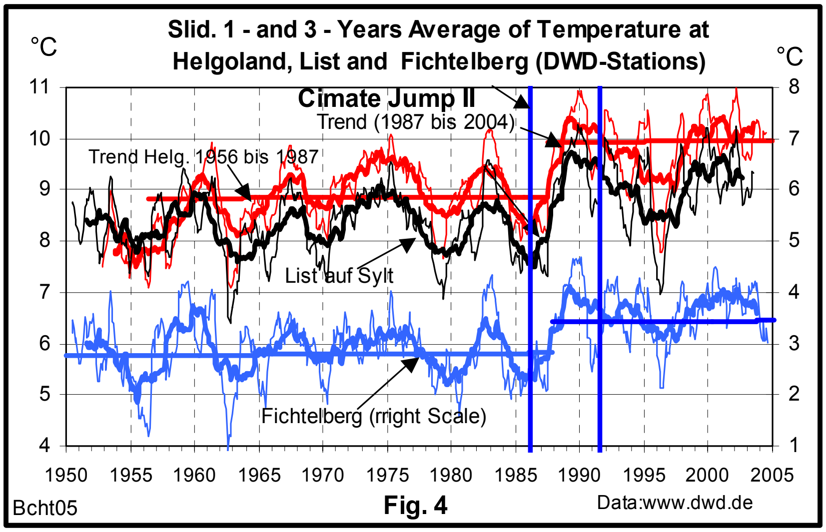


Fig. 4

The main increase in temperature in Central Europe happened between 1987 and 1990. From 1991 on until now the sliding yearly averages of the ground near temperatures oscillate around a level of approximately 0.8 °C to 1.5 °C higher than the old level. As an example Fig.4 shows the time rows of yearly averages of temperature at the islands Helgoland and Sylt in the North Sea in comparison with the Temperature at the high positioned DWD-Station of the Fichtelberg in Central Europe.

Sliding yearly averages of the temperature show an oscillation period of about three years. Therefore the sliding three years averages demonstrate the jump of temperature between 1987 and 1992 much clearly.

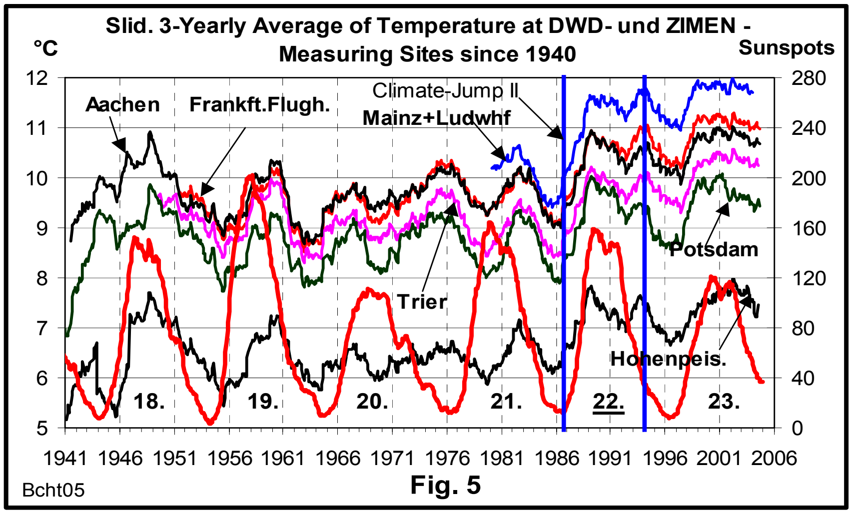


Fig. 5

Fig.5 shows the climate jump of some measuring sites in Central Europe. Absolute temperatures on mountains (Hohenpeissenberg) are lower than in valleys but all stations show the same trend. There one can find an opposite correlation between the temperature differences during the jump with the high of measuring points above NN. The curves of temperature are shown in comparison with the yearly numbers of sunspots since 1941 (Cugnon P., 2005). The jump of the temperature at all stations, called "Climate Jump II", happens with in the 22nd Sun spot period, which appeared between 1986 and 1996. During this time Earth was influenced by a lot of very strong extraterrestrial events (Thompson R., 2004), (STEDATA 22, 2003).

Tropospherical O3, Global Radiation, Sunshine and Clouds

To seek for causes of the new forest decline measurements of air pollution and meteorological components had been started since 1984 at fife forested background stations in Rhineland-Palatinate. Since this time were measured global radiation and O3. O3 is mainly produced by photolysis of the anthropogenic precursor NO2 in presence of Hydrocarbons in traffic regions and towns. It is transported into the forested regions far away from these anthropogenious precursors..

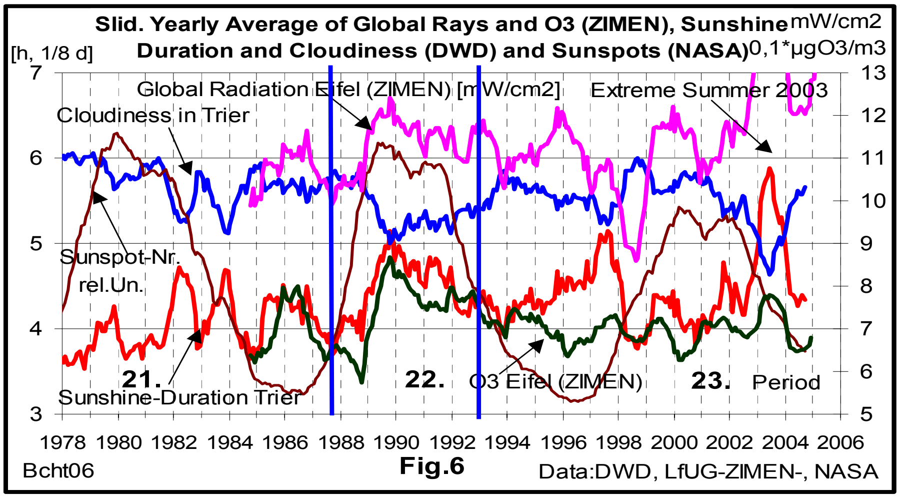


Fig.6

The strong increase of O3 in the short period between 1987 and 1990 mainly is caused by the strong increase of global radiation. After 1990 O3 was decreasing continuously as a consequence of the reduction of anthropogenic precursors by controlling the emissions of cars (ASU-controlling) and legal introduction of the controlled catalyst. Today the yearly averages of O3 are nearly constant in towns and forests at a relative low level. Yearly averages in towns are about the half of that in the forested background stations. Sliding yearly averages of sunshine duration corresponds nearly with Global Radiation (Fig.6). Naturally inverse are the time rows of cloudiness. Strong alternations of all components happen between about 1988 and 1991. The yearly averages of Global Radiation were increasing during this short time about 1.5 mW/cm3 and caused an increase of the yearly averages of temperature of about 1.2 +- 0.3 °C. The Global Radiation is strongly modulated by Cloudiness. Therefore one must look fore possible influences on Cloudiness, which steers Sunshine and in consequence anthropogenuous O3 and Temperature. These strong alternations of all components were lying in the time range of the 22nd Sunspot period with its already mentioned extreme terrestrial influences. Therefore one should seek for possible links between Sunspot frequencies and terrestrial meteorological components.

Sunspots and Neutronrates

According to a theory of Marsh and Svensmark (Eur. Org. for Nucl. Res. CERN, 2000) secondary particles of the extragalactic cosmic rays produce clouds in air saturated with water like in a **Wilson Fog Chamber** (1911). To study the production of these secondary particles of cosmic rays several physical institutes worldwide are measuring the neutron rates since 1958 (World Data Centre C2, 2005). Besides other Particles Neutrons are formed through nuclear collisions of extra galactic cosmic radiation interacting with the atmosphere. They represent the intensity of secondary particles and are relative easy to measure. A comparison with the sunspot frequencies shows, that there is a reduction of neutron flux during the maximum of each sun spot period. The frequency of Sun spots influences the intensity of cosmic rays. If the secondary particles of cosmic rays would produce clouds, than exists a link between sun activity and terrestrial climate change.

Neutron rates represent the intensity of secondary particles, which are condensation nuclei for clouds. Data collected from satellites also show that the amount of low clouds over the earth closely follows the amount of secondary particles of extra galactic cosmic radiation. Stronger solar wind during the maximum of sunspots shields the earth from extra galactic cosmic rays, therefore neutron rates are opposite correlated to the sunspot curve: Sunspots are accompanied by solar flares, which are the most energetic explosions in the solar system and have a direct effect on the earth's upper atmosphere, which becomes ionised and expands.

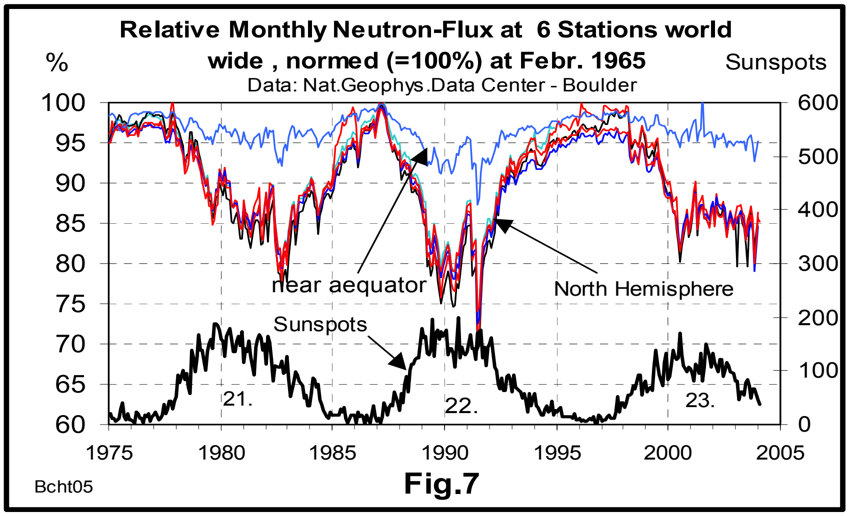
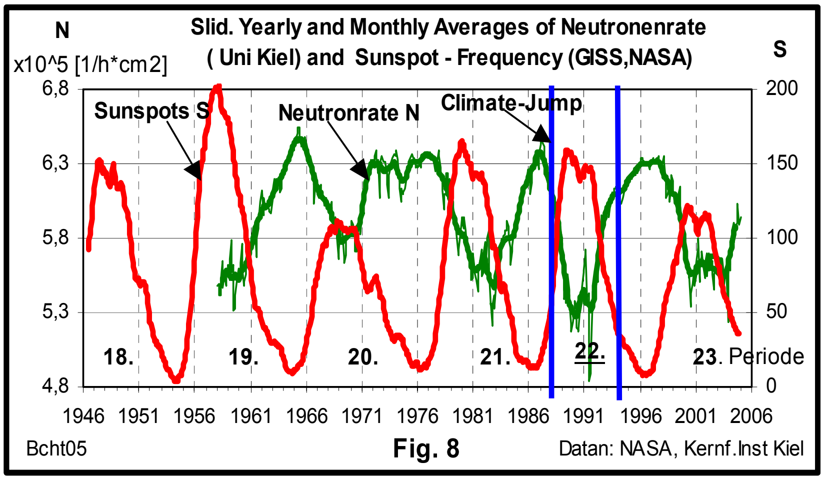


Fig.7

They are Roentgen Rays between 0.01 and 1 nm, reaching the Earth after 8 minutes and mark the starting point of the current of protons, which have velocities of more than 300 km/sec. The magnetic field of this "Sun wind" deflects the cosmic rays, which are high energetic protons, coming from extragalactic sources (so far as we know), and reduces the secondary particles in the lower atmosphere und on this way cloudiness. This effect depends on the number of sunspots and especially of their energetic efficiency. With this method the Sun opens its way to the earth and warms up the lower atmosphere.



Slid. Yearly and Monthly Averages of Neutronenrate (Uni Kiel) and Sunspot - Frequency (GISS,NASA)

Fig. 8

Datan: NASA, Kernf.Inst Kiel

This process works always und modulates the terrestrial climate. One can find harmonic correlations between the sun periods and the oscillating global temperatures (Scafetta and West, 2003). During the 22nd and actual 23rd period relative often extremely high energetic mass ejections were observed. They are to distinguish from all periods before 1986.

As a consequence of these high activities of the sun there are relative strong reductions of cosmic rays till about 30% of the monthly averages worldwide (Fig 7). Stations in the north of the 40th Latitude have nearly the same loss of cosmic rays and more than twice of equatorial places (Huancayo): Therefor it seems to be plausible that the averaged increase of global temperature is smaller in the equatorial region (0.5 to 1 Degree C/100 Years) than in the northern hemisphere (2 to 4 Degrees/100 Years) (Gray, V.R., 2003).The time rows of the Neutron rates, measured by the Institute of Physics of the University in Kiel are very good negative correlated with the time rows of the sunspot frequency (Roehrs, 2005) (Fig.8).

Neutron Rates and Cloudiness

During the 22nd Period we had a very strong reduction of cosmic rays and clouds.

A rough estimation gives, that the reduction of the Cosmic Rays of about 17 % may lead to a reduction of Cloudiness of about 13 %. During the Climate Jump this gives an increase of the averaged yearly ground near temperature of about 1.2 +- 0.3 °C in Europe.

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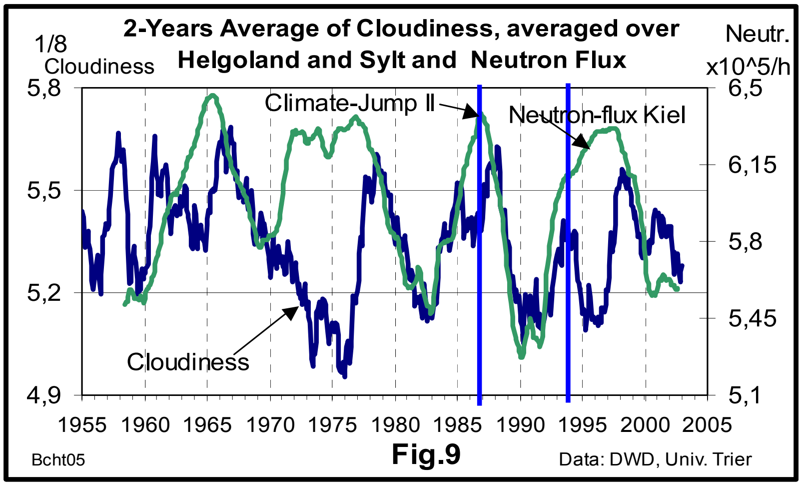


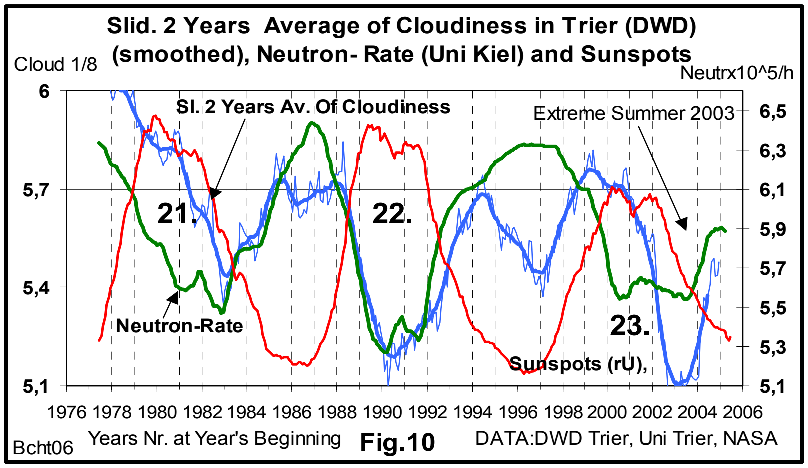
2-Years Average of Cloudiness, averaged over Helgoland and Sylt and Neutron Flux

Bcht05 **Fig.9** Data: DWD, Univ. Trier

This correlation between cloudiness and cosmic rays is the link of the controlling connection between sun activity and terrestrial climate change.

One finds this correlation at all measuring sites of the DWD, for instance at stations direct at the cost in the Northern See (Fig.9) and in the south of Germany near the Alps.

Some deviation of this rule happens between 1970 and 1978, but it seems to be a greater part of systematic delaying effect: After each main reduction of cloudiness which is correlated with reduction of cosmic rays, exists nearly systematic a delayed short time reduction of cloudiness. These "delayed reduction" seems to be caused by another meteorological influence, which is modulated by sun activity, for instance the North-Atlantic Oscillation. (NAO). Between Changes of Neutron flux, representing secondary particles of Cosmic radiation, and Changes of cloudiness seems to be a delaying time. Using a delay-time of 1 year, one gets an correlation factor of 0.8 between Neutron rates and cloudiness in Potsdam.

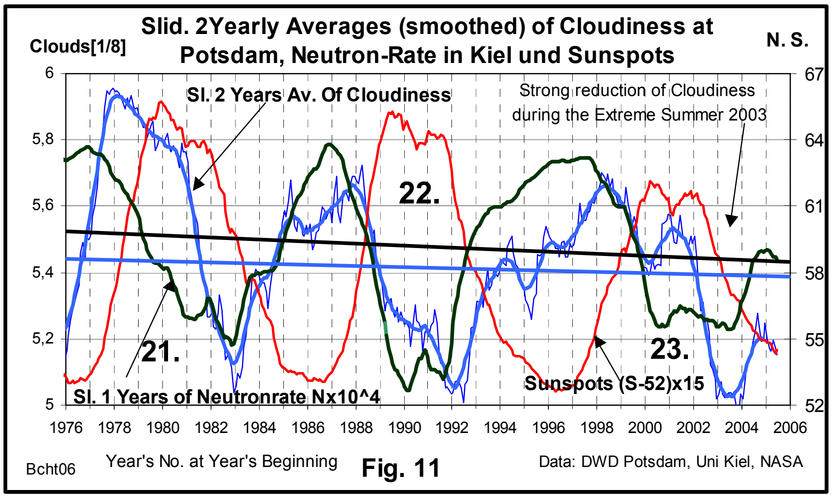


Slid. 2 Years Average of Cloudiness in Trier (DWD) (smoothed), Neutron- Rate (Uni Kiel) and Sunspots

Bcht06 **Fig.10** DATA:DWD Trier, Uni Trier, NASA

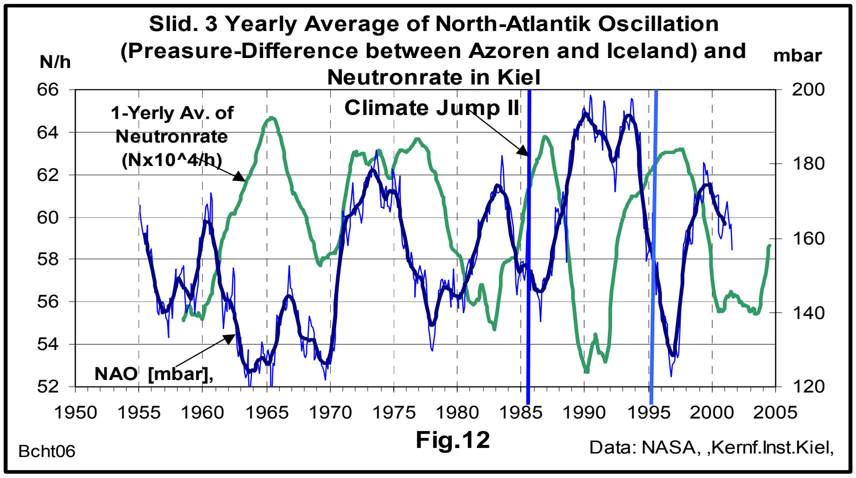
Therefore one could suppose, that cloudiness will be really influenced by drops producing cosmic rays (micro aerosols), delayed by the inertia of the oceans..

This supposition seems to be stabled by similar behaviour of the long time trends of neutron flux and cloudiness (Fig.11)



North Atlantic Oscillation (NAO) and Sun Activity

Locking for other data to support this theory one can find an relatively strong anti correlation between the time rows of the North Atlantic Oscillation (NAO) and Neutron rates especially since about 1980, when global Temperature starts to increase the second time in the last century (Climate Jump II). The NAO shows the time rows of the Difference of Air Pressure measured at Azore - Islands and at Iceland



The opposite correlation between the NAO and Neutron rate in Fig. 12 gives rise to the opinion, that cosmic radiation influences via Swensmark- effect the NAO and by this the climate in Central Europe.

There exists a relatively strong correlation between the North - Atlantic- Oscillation and the behaviour of the weather in Central Europe, for instance the cloudiness (Fig. 13).

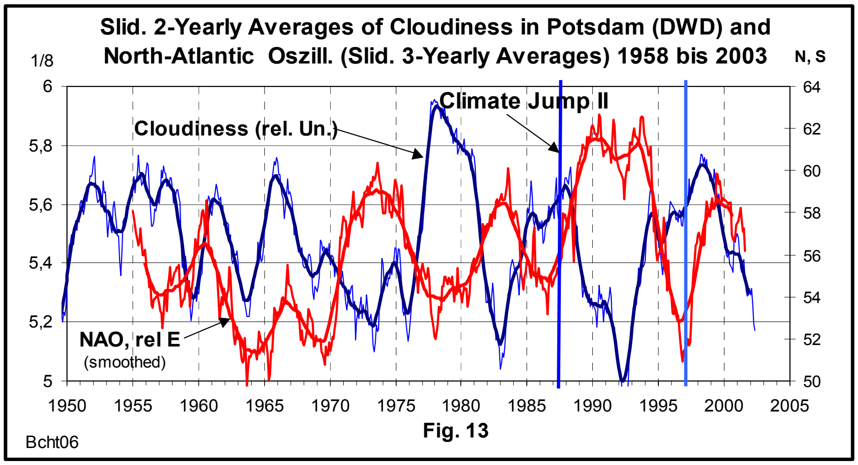


Fig. 13

Further more we can find a relative good correlation between sunspots and NAO (Fig. 14). Between the periodic changing sun activity and its influence on the earth's meteorology one can observe a certain delay-time of about one year, possibly caused by the inertia of the ocean.

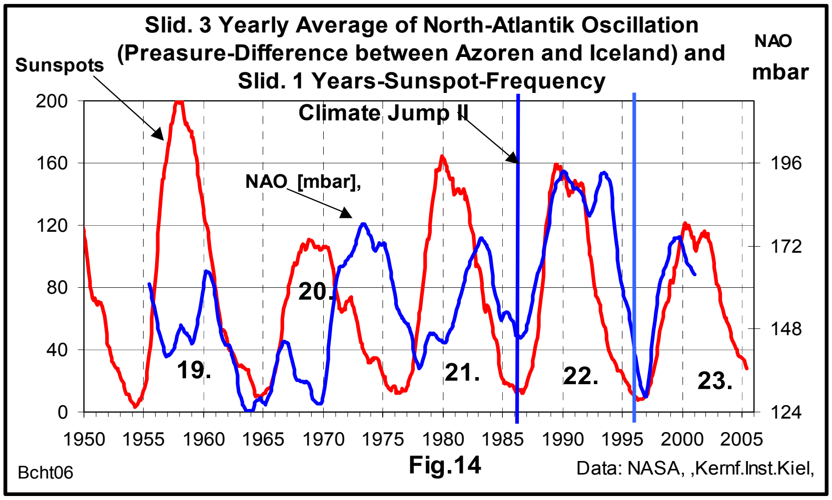


Fig.14

Data: NASA, ,Kernf.Inst.Kiel,

Cosmic Rays, Temperature and Growing Season

Time rows of temperature averaged over 4 DWD-stations in Central Germany are in wide time ranges similar to periodic alterations of Sun spot frequencies. Further they are in opposite correlation to Cosmic Radiation (Fig.15), which is good correlated with cloudiness (Fig.10). On this way there seems to be a causal chain between sun activity and development of terrestrial temperature: The strong alterations of air pollution and climate components between 1986 and 1991 seems to be a consequence of a not normal increase of sun activities with strong reducing cloudiness and increasing sun shine. During this climate jump ground level temperature increases relatively strong (about 1,2 °C +- 0,3 °C) and remains at higher long time level up to now.

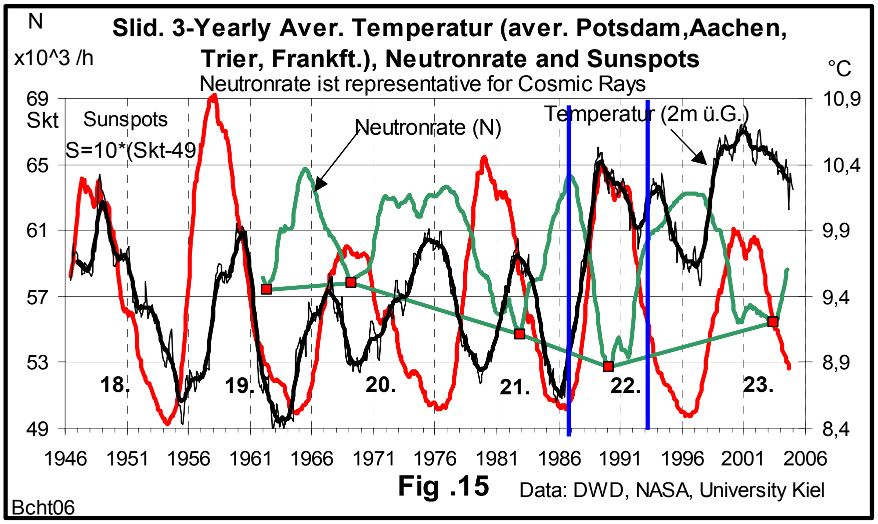


Fig .15 Data: DWD, NASA, University Kiel

As a consequence of this Climate Change at the end of the eighties one can observe a strong influence into biological systems: Fig.16 shows a correlation between the Reduction of Starting time of growing season in Central Europe and decreasing Neutron rates.

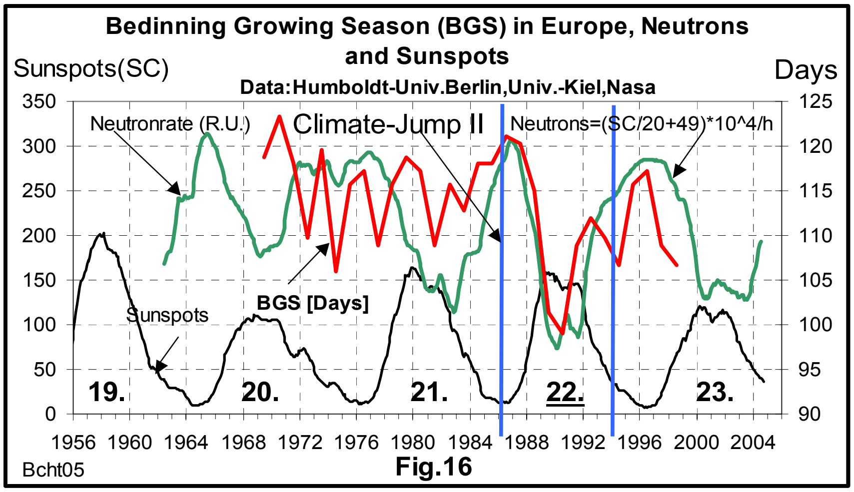


Fig.16

The prolongation of the greening time of Plants (Chmielewski, F.-M. and Rötzer, T.)

starts just with the strong reduction of Neutron Rays with beginning of the 22. Sunspot period. The Growing Season seems to be controlled by Sun activities.

Sun Emissions of Protons

To look for further observations to stable the sun made climate change during the eighties we studied by NASA published satellite measurement values. Fig 17 shows the monthly satellite-measured sums of Protons with energies higher than 10 MeV and per cm2 and sterad. These strong "Sun Winds" started during the 22nd Period 1989 with an extremely large sunspot in March and continued in October with great solar mass ejections. These proton currents produced blackouts at electric power plants in the northern hemisphere, like USA, Canada and Sweden, they disturbed wireless contacts between earth and aeroplanes and satellites, they produced auroras seen at the Equator. Such strong solar mass ejections occurred repeatedly during the 22nd and in the 23rd period until now. The NASA comments this behaviour "The Sun Goes Haywire". One of the last great sun wind events influencing earth occurred at the 15 January 2005 from a sunspot Nr. NOAA 720.

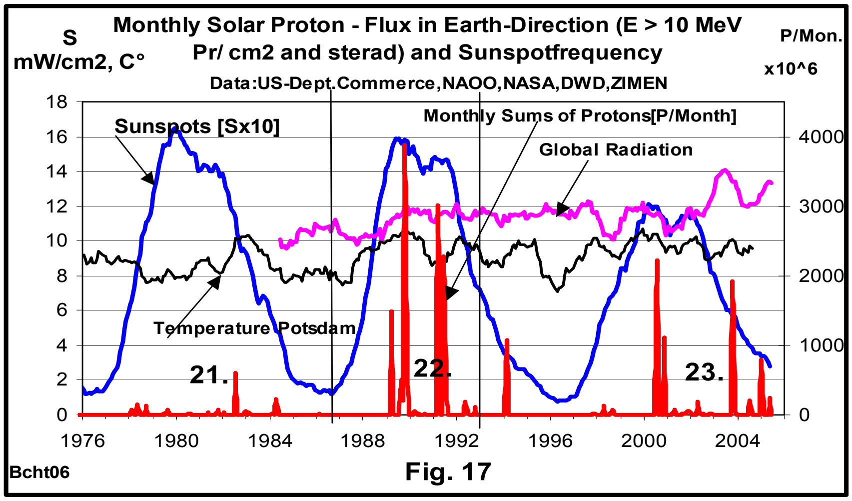


Fig. 17

This behaviour of the sun makes the fact plausible that temperature remains in tendency at a higher level than before 1988.

Global Temperature and Sunspots

This work deals with the question of the global warming: There is no continuous increase of global temperature since 1900, whereas the time rows of global temperature show two jumps since 1900: The first “Climate-Jump I” happens between approximately 1920 and 1935, the second “Climate Jump II” from 1989 to about 1994 (Fig. 14). The second is caused by special solar activities like described in this paper.

Some other observations point to extraterrestrial influences of climate change: The 11 Years averaged Sunspot periods are increasing until 1960, than they are nearly stable until now.

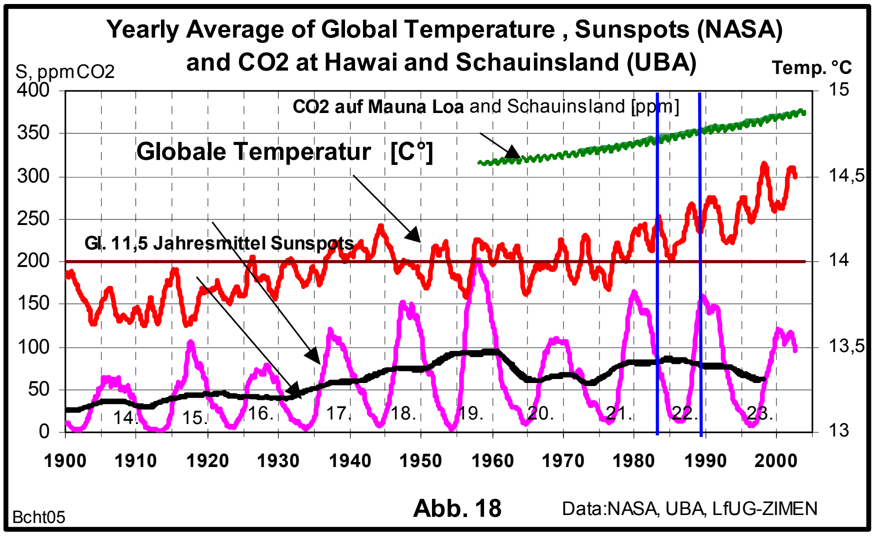


Abb. 18

Data:NASA, UBA, LfUG-ZIMEN

The trend of global temperature increases with decreasing length of the basis of sunspot periods. The Index of the North Atlantic Oscillation (NAO) shows during Climate Jump II (1989 - 1992) a strong anomaly. The increase of CO2 is continuous and shows no jump. One can find a modulation of the increasing averages of the CO2-concentration of Hawaii by the 22nd Sun spot period. It seems to be possible, that the increasing CO2 concentration is powered by increasing sun activity too. The main cause of the sudden climate change during the eighties was the sudden increasing number of extreme height energetic mass ejections of the sun, surely caused by a special nearby constellation of the torques of the Sun and Sun System (Landscheidt Th., 2004). Further studying these phenomena with further measured data may lead also to answer the question, why the global warming seems to tend today to lag behind the increase in greenhouse gases.

Conclusion

In the last thirty years the main change of measured air pollution in Central Europe happened within the short period of 4 years between 1987 and 1991. The climate change happened during the same time interval. These events coincided with increasing sun activities, increasing intensities of sun winds and with decreasing cosmic radiation (neutron rates) with the consequences of reducing cloudiness, increasing global radiation and increasing ground near temperature. The conclusion is, that since about 1940 mainly with starting of the 22nd Sun spot period climate changed in Central Europe, which strongly influenced transportation (SO2, Dust, NO2, O3), air chemical production (O3) and concentrations of air pollution. Correlations between changes of the North Atlantic Oscillation and Cosmic Radiation point to a strong controlling influence of sun activity (Sunspot frequency and intensity of Sun Winds) to terrestrial climate change.

References

Borchert, H., 1998. The Trend of Air Pollution in Western Germany in the past Twenty Years as a Result of Clean Air Management, 11th World Clean Air Congress IUAPPA, Durban, S.Africa, ISBN 0-620-23064-9. www.UMAD.de

Borchert, H., 2004. Changes of Air Pollution in Central Europe in Correlation with Changes of Climate and Sun Activities, 13th World Clean Air Congress, London, August 2004, Nr.39, CD, www.UMAD.de.

Chmielewski F.M.; Rötzer, T., 2000. Phenological Trends in Europe in Relation to Climate Change, Agrarmeteorologische Schriften, Heft 07,2000, Humboldt-Universität Berlin, www.agrar.hu-berlin.de/pflanzenbau/agrarmet

Cugnon, P. et al., 2005. Online catalogue of the sunspot index, sidc.oma.be

Deutscher Wetterdienst, 2005: Data of temp., cloudiness, sunshine: www.dwd.de.

European Organisation for Nuclear Research, 2000, A Study of the Link between Cosmic Rays and Clouds with a Cloud Chamber at the CERN PS, CERN/ SPSC 2000-021,P317, Apr. 24. 2000, xxx.lanl.gov/abs/physics/0104048.

Gray V. R., 2003. Regional Temperature Change. www.john-daly.com/guests/regional.htm.

Marsh, N. and Svensmark, 2000.Cosmic Rays, Clouds, and Climate. Space and Science Reviews. pp 1-16, Kluver Acad. Publishers. www.dsri.dk.

NASA, 2004. Record-setting Solar Flares"; www.spaceweather.com/solarflares.

Roehrs, 2005 : Ergebnisse. der Kieler Neutronen-Monitor-Messung. ifkki.kernphysik.uni-kiel.de.

STEDATA 22, 2003. Database for 22nd Solar Activity, Dep. of Earth Science, Baraki University: shnet1.stelab.nagoya-u.ac.jp/omosaic/step/stedata.htm.

Scafetta, N., West, B. J., 2003. Solar Flare Intermittency and the Earth's Temperature Anomalies. Phys. Rev. Lett. 90,248701

Landscheidt, Th. 2004. Klimavorhersage mit astronomischen Mitteln? Schroeter Institut, Research in Cycles of Solar Activity, Nova Scotia, Canada, www.solidarität.com

Thompson, R. 2003. Solar Cycle Number 22 (1986 – 1996) in Review, Australian Government, IPS Radio and Space Services: www.ips.gov.au/Educational/2/3/2

World Data Centre C2 for Cosmic Rays, www.env.sci.ibaraki.ao.jp/data

Zentrales Immissionsmeßnetz (ZIMEN): Data from 1978-2000: Monthly bulletins ISSN 0720-3934; Since 2001: www.UMAD.de